INTRODUCTION TO THE PHYSICS OF ATOMS, MOLECULES AND PHOTONS (BENEDICT)

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Introduction to the Physics of Atoms, Molecules and Photons

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CHAPTER OVERVIEW

Introduction

These lecture notes have been prepared to give an introduction into the foundations of atomic and molecular physics with an emphasis on the interaction of these atomic systems with light, and in more general, with electromagnetic fields. The character of the material is theoretical, and wishes to rely on theoretical mechanical and electrodynamical studies of the students, which is a prerequisite of being able to follow the material presented here. This is an advanced course for BSc students. In spite of the theoretical approach based on mathematical argumentations, we tried to connect the material with experimental observations. These short notes, however cannot be considered as a replacement of courses where deeper experimental insight should be gathered.

There are several problems (~50) embedded in the text, and their solution is strongly recommended for the students. In view of the author this is a necessary condition for getting a reliable knowledge of the subject, as is the case with any other physics subject. The electronic form made it possible to include animations which may significantly improve the level of understanding, as it enabled us to couple demonstrations and interactive animations to the material which should make more easy the understanding of the rather abstract notions and laws of atomic physics. These are – as it is usual in physics – quantitative relations, the true depth and content of which can only be understood in the language of mathematics. This difficult task is intended to be promoted by the included multimedia materials. The animations can be started by clicking on the links in the tables, which visualize the problems in question.

The theory of atomic and molecular physics is not an easy subject, but modern technology is based more and more on the laws and properties of micro-world, so it seems necessary to understand the most important rules and methods of this field of a physics student.

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1: Wave-corpuscular duality of photons and massive particles

Objectives

In this chapter we review the main experimental results showing the dual behaviour of light. In the last section the concept of probability amplitude playing a keyrole in quantummechanics is introduced

Prerequisites

Elements of classical mechanics, interference of light. Elements of calculus and probability theory. The concept of probability distribution.

The double slit experiment with light

The nature of light, whether it consists of corpuscles or is it a wave of an unidentified medium, called ether, intrigued scientists for a long time before the beginning of the 20th century, and there was a long standing dispute between the two views. A seemingly final solution came along with the numerous interference experiments in the beginning of the 19th century performed by Thomas Young, Augustine Fresnel and others, which had shown the wave nature of light. Here we present the double slit experiment of Young. It is interesting that about a 100 years later in 1909 Geoffrey Taylor repeated the experiment with a very weak beam that resulted in the same fringes after a sufficiently long time.

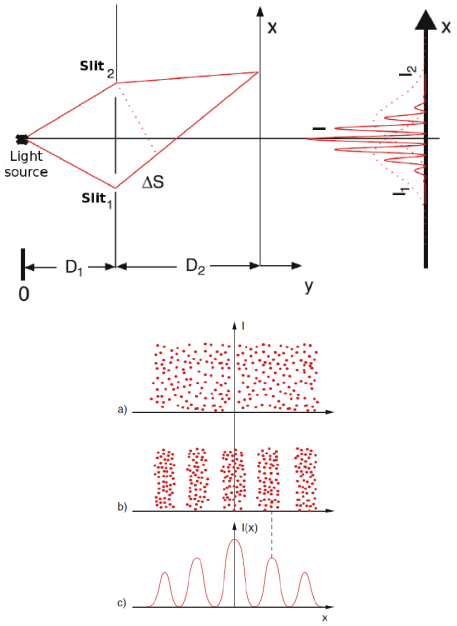


Figure 1.1: The double slit experiment of Young. Secondary light waves emerging from the two slits show interference fringes on the screen along the *x* direction. This was considered for a long time as the proof of the wave nature of light.

The photon hypothesis

It turned out however, that nature is more complicated than simple man's imagination. The first step towards a deeper understanding of what light is was done by Max Planck in 1900. In order to explain correctly the spectral distribution of radiation emitted from a hot body like the sun, or a heated piece of iron, he had to assume that light waves emerging from the body took up energy from it **in quanta**. The smallest amount of quantum is determined by the frequency ν of the emitted light and a universal constant h so that a single quantum has

$$\varepsilon = h\nu \quad (1.1)$$

energy, where the requirement to be in agreement with the experimental observations determined the value of

$$h = 6.63 \times 10^{-34}\text{Js} \quad (1.2)$$

called the Planck constant. This is an extremely small value therefore even for visible light the energy of a single quantum is only of the order of 10^{-19}J, that is why we do not observe this granular property of light.

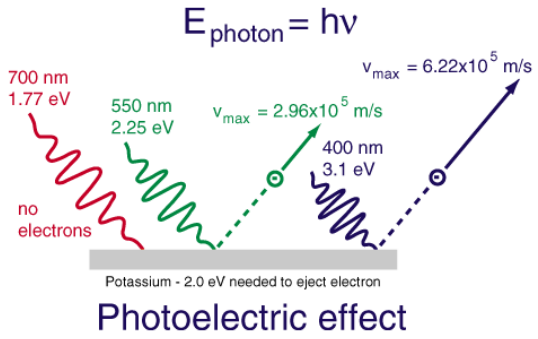


Figure 1.2: Schematic drawing demonstrating the photoelectric effect. http://hyperphysics.phy-astr.gsu.edu/hbase/mod1.html

The next fundamental step was when A. Einstein extended Planck's ideas to the explanation of the photoelectric effect discovered by Hallwachs and Stoletov and studied in detail by P. Lenard and Herz. If light falls on the surface of a metal, it becomes positively charged. The reason for this is that electrons i.e. negatively charged particles called photoelectrons are emitted from the surface of the metal. On the details of this phenomenon we refer here to courses of experimental physics. The observations were explained by Einstein, by the assumption that the electrons in the metal absorb the energy of the light field in quanta. Following the idea of Planck, Einstein assumed that the energy of a single light quantum is

$$\varepsilon = h\nu \quad (1.3)$$

where ν is the frequency of the light, h is Planck's constant. A frequently used notation is

$$\hbar = \frac{h}{2\pi} \quad (1.4)$$

and with the angular frequency $\omega = 2\pi\nu$ we can write Einstein's relation as

$$\varepsilon = \hbar\omega \quad (1.5)$$

which is used more often is theoretical physics. The energy quantum of light obtained the name *photon*. The kinetic energy of the emitted electrons is given by the following equation:

$$E_{kin} = h\nu - W_a \quad (1.6)$$

where W_a – called "work function" – is the energy needed to extract the electron from the metal, which is characteristic for the metal. If $h\nu$ is smaller than W_a, there is no electron emission. For alkaline metals Na, Cs even visible light shows the effect, while for most metals the threshold frequency determined by $h\nu_t = W_a$ falls into the ultraviolet region.

The assumptions of Einstein were proven exactly later by experiments of Millikan in the photoelectric effect. The value of E_{kin} can be determined by the countervoltage U_0 given to the electrode registering the electrons. The value of q_0U_0 – where q_0 is the electron's charge – that stops the electrons gives W_a. Eq. (1.6) is Einstein's photoelectric equation, which can be proven plotting U_0 versus the light frequency ν.

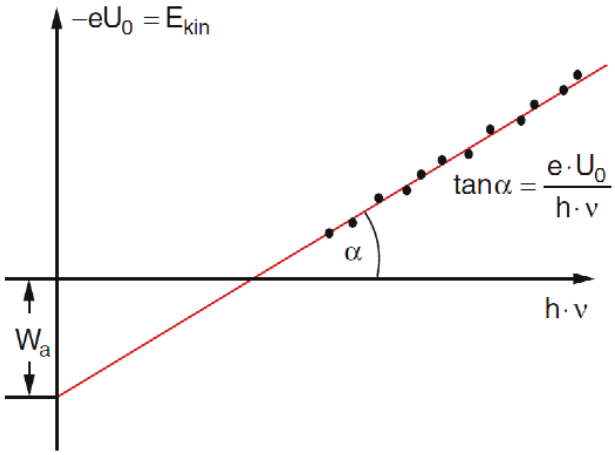
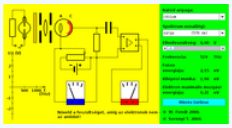


Figure 1.3: Plotting countervoltage U_0 versus the light frequency ν.

Animation



The photoelectric effect can be investigated with this simulation. A virtual experiment can be performed to determine the Planck-constant and the "work function" W_a.

http://www.walter-fendt.de/ph14e/photoeffect.htm

Photon momentum

According to Einstein the photons must posses not only energy but momentum, as well: A light quantum with frequency ν, whose wavelength in vacuum is $\lambda = c/\nu$, has momentum

$$\mathbf{p} = \frac{h\nu}{c}\hat{\mathbf{k}} = \frac{h}{\lambda}\hat{\mathbf{k}} = \hbar\mathbf{k} \quad (1.7)$$

where $\hat{\mathbf{k}}$ is a unit vector pointing in the direction of the propagation of light field which is assumed to be a monochromatic plane wave, $\mathbf{k} = k\hat{\mathbf{k}}$ is the vector called wave-number with absolute value $k = 2\pi/\lambda$. This value of $\mathbf{p}$ is in accordance with the fundamental relation of relativity, valid for any particle of rest mass m_0:

$$E^2/c^2 - p^2 = (m_0 c)^2 \quad (1.8)$$

assuming that the photon's rest mass is m_0=0.

The Compton effect

Among the several evidences of the photon hypothesis a very important one is the Compton effect, which is seen in figure 1.4. In this experiment, performed by Arthur Compton, an X ray of wavelength λ_0 falls on a sample and ejects electrons from it. There appear also a secondary X ray, whose wavelength λ_s and direction, given by the angle φ is different from the original one. These can be measured by the experiment shown in the figure 1.4.

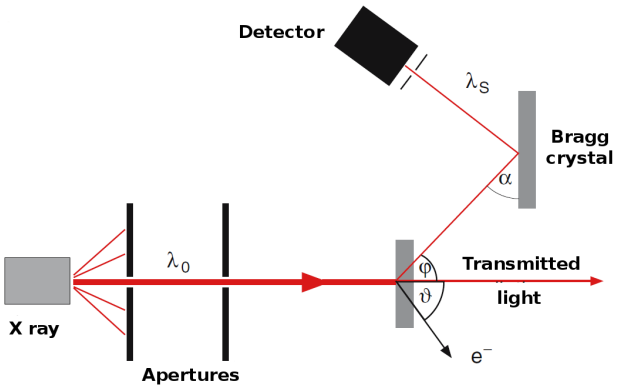


Figure 1.4: Experimental setup for the Compton scattering experiment.

We can consider the effect as the scattering of the photon on the electron where both of them are classical point-like objects. The conservation of energy and momentum requires:

$$\begin{aligned} h\nu_0 + E_0 &= h\nu_s + E_e \\ \frac{h\nu_0}{c} &= \frac{h\nu_s}{c}\cos\varphi + p_e\cos\vartheta \\ 0 &= \frac{h\nu_s}{c}\sin\varphi - p_e\sin\vartheta \end{aligned} \quad (1.9)$$

Here $E_0 = m_e c^2$ is the rest energy of the electron, E_e and p_e are the energy and momentum of the electron after the collision

$$E_e = \frac{m_e c^2}{\sqrt{1-v^2/c^2}}, \quad p_e = \frac{m_e v}{\sqrt{1-v^2/c^2}} \quad (1.10)$$

according to the relativistic formulas.

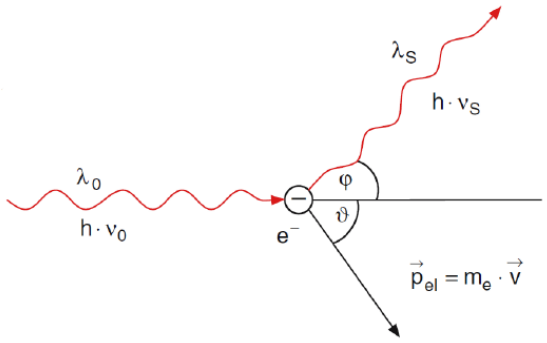


Figure 1.5: The X ray photon approaching from the left is scattered on the electron.

Both of them are treated as classical point-like objects From the three equations above, and using $\nu = c/\lambda$ we get with some algebra the result

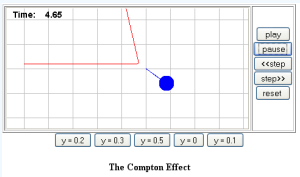
$$\lambda_s - \lambda_0 = \frac{h}{m_e c}(1-\cos\varphi) \quad (1.11)$$

(Strictly speaking the result is valid for free electrons in rest. In the experiments the electrons are set free from atoms, where they have some negative binding energy, but this can be neglected compared to other energies occurring here.) The expression above connects the change of the wavelength of the X ray photon during the scattering and the scattering angle φ. Compton's experiments approved the theoretical result. The length

$$\lambda_C = \frac{h}{m_e c} = 2.43\times10^{-12}\ \mathrm{m} \quad (1.12)$$

is called the Compton wavelength of the electron. Note that sometimes the value $\tilde{\lambda}_C = \frac{\hbar}{m_e c} = \frac{\lambda_C}{2\pi}$ is called the Compton wavelength.

Animation



Study the Compton effect with the animation on the page and answer the questions appearing there.

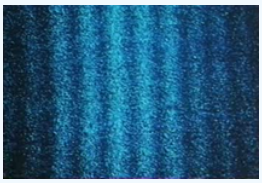
http://physics.bu.edu/~duffy/semeste...5_compton.html

According to these experiments the electromagnetic field can manifest itself of being of discrete nature, and for a given frequency and direction of propagation, it interacts as a particle with atomic matter with the corresponding energy and momentum.

Probability waves for massive particles

After the photon hypothesis had proven to be true, many physicists tried to reconcile the two views, how it is possible that light behaves as a kind of a wave, whereas it consists of quanta or particles that have energy and momentum. While these attempts were not successful, another view emerged. L. de Broglie a French physicist set up the hypothesis that perhaps the behaviour of the electrons in atoms can be explained, if one assumes that electrons – that were known to be massive particles and possessing well defined negative charge – might also behave like waves. Later on, this assumption was proven experimentally by G. P. Thomson, and independently by Davisson. The property that an electron just like photons can behave either as a particle or as a wave is called duality. This very unexpected property was resolved by Max Born in 1926 by purely theoretical arguments. But before explaining Born's idea, let us turn to an experiment revealing explicitly the duality property. This is the famous double slit experiment – one of the most interesting experiments in physics – first performed with electrons by Clauss Jönsson in 1961 and popularized later by Akira Tonomura.

Animation



The experiment seen in Fig. 1.6 was first performed by Clauss Jönsson in 1961. A famous variant of the experiment was done by Akira Tonomura, he made the result visibly available, the video of which is shown here.

http://titan.physx.u-szeged.hu/~mmqu...eslitTono.mpeg

Looking at the experiment in more detail, it turns out that the picture is formed by individual pointlike impacts of particles, as it is seen in the sequence of figure 1.6. A result definitely different from the case of water waves.

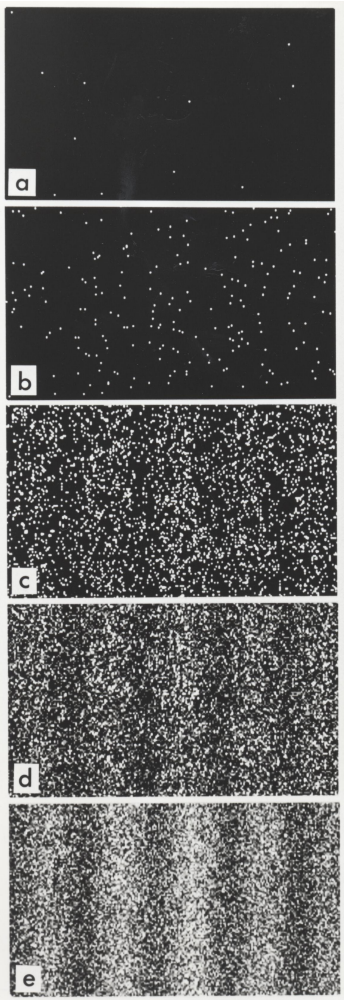


Figure 1.6: Result of the double slit experiment with electrons. Sequence of figures a, b, c, d, e shows the electrons reaching the screen with increasing exposition time. The interference pattern is formed by individual pointlike impacts of the particles. To understand the wavelike behaviour of quantum particles it is necessary to introduce a probabilistic interpretation.http://commons.wikimedia.org/wiki/Fi...Tanamura_2.jp

This extraordinarily surprising phenomenon can be explained with the fundamental concept of quantum mechanics: called the **probability amplitude**. We shall consider only one of the coordinates, the *x* coordinate which is perpendicular to the fringes seen on the screen where the particles are detected. We do not know exactly what was the state of the particle before arriving at the screen. This state will be denoted by ψ. But we know that after falling on the screen we realize that it is at a place say x_1. This event will be characterized by a complex number to be denoted by $\langle x_1 \mid \psi \rangle$. So to each *x* we attribute a complex number $\langle x \mid \psi \rangle$. Considering all the possible *x* values we get a function of *x*, which is a complex valued function of the real variable – the position of the particle – *x*:

$$\langle x \mid \psi \rangle = \psi(x) \quad (1.13)$$

This function will be used to characterize the state of the particle, and this function is called the **coordinate wave function**. The important law of quantum mechanics is that the probability of finding the particle around *x* in a small interval *dx* is $|\psi(x)|^2 dx$. In the language of probability theory, $|\psi(x)|^2$ is the probability density function of the coordinate of the particle which is a random variable. So we have

$$|\langle x \mid \psi \rangle|^2 = |\psi(x)|^2 = \psi^*(x)\psi(x) =: \rho(x) \geq 0 \quad (1.14)$$

In quantum mechanics we use the notation $\rho(x)$ for the probability distribution. The probability of finding it at a point *x* in the interval $x_1 < x < x_2$ is given by:

$$P\left(x_1 < x < x_2\right) = \int_{x_1}^{x_2} |\psi(x)|^2 dx = \int_{x_1}^{x_2} \rho(x) dx \quad (1.15)$$

which is valid for arbitrary $x_1 < x_2$. The probability of finding the particle somewhere on the real axis must be 1, therefore:

$$\int_{-\infty}^{\infty} \rho(x)dx = \int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad (1.16)$$

Accordingly the wave function describing a particle must be such that the integral of its absolute value square between $-\infty$ and ∞ should give 1.

The interference pattern seen in Fig 1.6 can be explained by the rules of quantum mechanics, as we shall do it in the following. The particle which was assumed to be in a state ψψ can arrive to the first slit on the screen, and this state, i.e. particle in the first slit will be denoted by ψ_1. The corresponding amplitude is then $\langle \varphi_1 \mid \psi \rangle$. Continuing its path it arrives somewhere to the second screen, where it is registered at the point *x*. The amplitude corresponding to this second part of its way is $\langle x \mid \varphi_1 \rangle$. The total amplitude belonging to the process that the particle arrives at xx through slit 1 is the product of the two amplitudes $\langle x \mid \varphi_1 \rangle \langle \varphi_1 \mid \psi \rangle$. Similarly, the amplitude of the other possible path of the particle, that it went through slit 2 before arriving at *x* is $\langle x \mid \varphi_2 \rangle \langle \varphi_2 \mid \psi \rangle$, where ψ_2 is the state of the particle, when it is at the second slit. The total amplitude is the sum of the amplitudes of the two possible paths.

$$\begin{aligned} \langle x \mid \psi \rangle &= \langle x \mid \varphi_1 \rangle \langle \varphi_1 \mid \psi \rangle + \langle x \mid \varphi_2 \rangle \langle \varphi_2 \mid \psi \rangle, \text{ or equivalently} \\ \psi(x) &= \varphi_1(x) \langle \varphi_1 \mid \psi \rangle + \varphi_2(x) \langle \varphi_2 \mid \psi \rangle = c_1 \varphi_1(x) + c_2 \varphi_2(x) \end{aligned} \quad (1.17)$$

where $c_1 = \langle \varphi_1 \mid \psi \rangle$, $c_2 = \langle \varphi_2 \mid \psi \rangle$. These latter amplitudes have been set to be two (complex) numbers instead of functions, because we have assumed here that the slits are small, and we need not distinguish between the different positions within the slits. What small means, will become more definite a little later. The sum of the amplitudes above is the superposition of the two possibilities. The probability of finding the particle at position xx is the absolute value square of the sum of the two possible amplitudes:

$$\begin{aligned} |\psi(x)|^2 &= |c_1 \varphi_1(x)|^2 + |c_2 \varphi_2(x)|^2 + c_1^* c_2 \varphi_1^*(x) \varphi_2(x) + c_1 c_2^* \varphi_1(x) \varphi_2^*(x) \\ &= |c_1|^2 |\varphi_1(x)|^2 + |c_2|^2 |\varphi_2(x)|^2 + 2\,\mathrm{Re}(c_1^* c_2 \varphi_1^*(x) \varphi_2(x)) \end{aligned} \quad (1.18)$$

The interference appears because of the last term. There will be places where the particles arrive with a small probability, these will be the dark fringes, whereas there will be places where the detection probabilities are large. Quantum mechanics gives the explicit form of the two functions $\varphi_1(x)$ and $\varphi_2(x)$, but we will not deal with this here.

We cannot tell which of the slits the particle went through, the interference pattern is the witness that it went simultaneously through both. It can be shown, that if we try to detect somehow which path the particle has taken, then a successful detection will destroy the interference pattern, so we cannot see simultaneously the interference pattern and distinguish between the two ways the particle went along. The same experiment has been performed with particles larger than electrons, like neutrons, atoms, small molecules. More recently the effect was demonstrated with the molecular object called fullerene, consisting of 60 Carbon atoms.

We did not emphasize so far, but it is important that the amplitude, i.e. the wave function depends also on time. If we wish to make use of time dependent wave functions we will denote it by a capital Greek letter: $\Psi(x,t)$. How does such a function look in any concrete case? This depends on the physical situation in question, and one of the important problems of quantum mechanics is to find the form of this function. In general we have to prescribe the property of square integrability with respect to *x*, because for any fixed value of the time variable *t* $|\Psi(x,t)|^2$ is the probability density of the coordinate of the particle. This interpretation of the wave function was first given by Max Born. Accordingly:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1 \quad (1.19)$$

at any time instant. We say then that $\Psi(x,t)$ is normalized to unity. This requirement will be (i) refined later and (ii) will necessitate certain prescriptions on how the wave function should depend on the time variable.

If we wish to give the position of the particle in three dimensional space, instead of the line, then the wave function shall depend on all three coordinates of the points in space: $\Psi(x,y,z,t) = \Psi(\mathbf{r},t)$. Here the random variable will be the position vector of the particle. The probability density is then the function $|\Psi(\mathbf{r},t)|^2$, for which the normalization is prescribed in three dimensions.

Max Born (1882-1970)

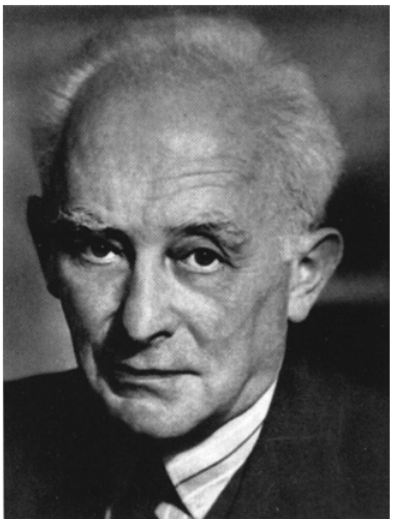


Figure 1.7:

Coming back to one dimension, a frequently used wave function (real in this specific case) for a particle localized more or less around the origin is $\psi(x) = \mathcal{N} e^{-x^2/4\sigma_0^2}$ at a given instant, where σ_0 is a constant independent of x, while $\mathcal{N}$ is a normalization factor. The corresponding probability density is $|\psi(x)|^2 =: \rho(x) = \mathcal{N}^2 e^{-x^2/2\sigma_0^2}$. Its integral along the real axis must give 1, this is the condition that determines the factor $\mathcal{N}$. As it is known from probability theory, this is the probability density of the so called standard normal, or Gaussian distribution function, if $\mathcal{N} = \left(2\pi\sigma^2\right)^{-1/4}$.

Problem 1.1

Show that the normalization factor in $|\psi(x)|^2 =: \rho(x) = \mathcal{N}^2 e^{-x^2/2\sigma_0^2}$ is $\mathcal{N} = \left(2\pi\sigma^2\right)^{-1/4}$.

According to what we said before, the function can depend on time as well, so that instead of σ_0 we can have a time dependent $\sigma(t)$ in it, and then of course (\mathcal{N}\) will be also time dependent. Besides the Gaussian wave function above there are many other possibilities depending on the physical problem in question.

Later on, we shall consider in detail the problem of the dynamics of the state, which means we shall consider how the state, i.e. the wave function changes with time given a force or a potential acting on the particle.

Problem 1.2

Investigating the photoeffect with a photocell where the cathode is covered by Cesium the electrons are stopped if the voltage is larger than 0.33V for a light wave of wavelength 546nm, while the corresponding value for 365nm is 1.46V. Derive the value of Planck's constant from these results. What is the work function of Cesium? How much is the stopping voltage using light of 436nm? What is the threshold wavelength producing electron emission?

Problem 1.3

Estimate the cost of one green photon in the case of a traditional 100W light bulb working with 5% efficiency, and switched on for 1 second.

Problem 1.4

Derive the result

$$\lambda_s - \lambda_0 = \frac{h}{m_e c}(1 - \cos\varphi) \quad (1.20)$$

for Compton scattering using the equations expressing conservation of energy and momentum:

$$\begin{aligned} h\nu_0 + E_0 &= h\nu_s + E_e \\ \frac{h\nu_0}{c} &= \frac{h\nu_s}{c}\cos\varphi + p_e\cos\vartheta \\ 0 &= \frac{h\nu_s}{c}\sin\varphi - p_e\sin\vartheta \end{aligned} \tag{1.21}$$

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2: Basic concepts of quantum mechanics

Objectives

In this chapter we introduce the Schrödinger equation, the dynamic equation describing a quantummechanical system. We discuss the role of energy eigenvalues and eigenfunctions in the process of finding it's solutions. Through the problem of linear harmonic oscillator the way one solves quantum mechanical problems is demonstrated. Finally the expectation value and the variance of an operator is discussed.

Prerequisites

Elements of differential equations, and the material of Chapter 1. The classical equations of motions. The classical harmonic oscillator.

The Schrödinger equation

As we have seen in the previous section, the state of a particle in position space is described by a wave function $\Psi(x,t)$ in one, or $\Psi(\mathbf{r},t)$ in three dimensions. This is a probability amplitude, and $\Psi(\mathbf{r},t)|^2$ is the probability density of finding the particle somewhere in space around the position given by the vector **r**. It was Erwin Schrödinger who wrote up the equation, the solutions of which gives us the concrete form of the function. His fundamental equation is called the time dependent Schrödinger equation, or dynamical equation, and has the form:

$$i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}=-\frac{\hbar^2}{2m}\Delta\Psi(\mathbf{r},t)+V(\mathbf{r})\Psi(\mathbf{r},t) \quad (2.1)$$

To simplify the treatment we consider in this subsection the one dimensional motion along the x axis:

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t) \quad (2.2)$$

Erwin Schrödinger (1887-1961)

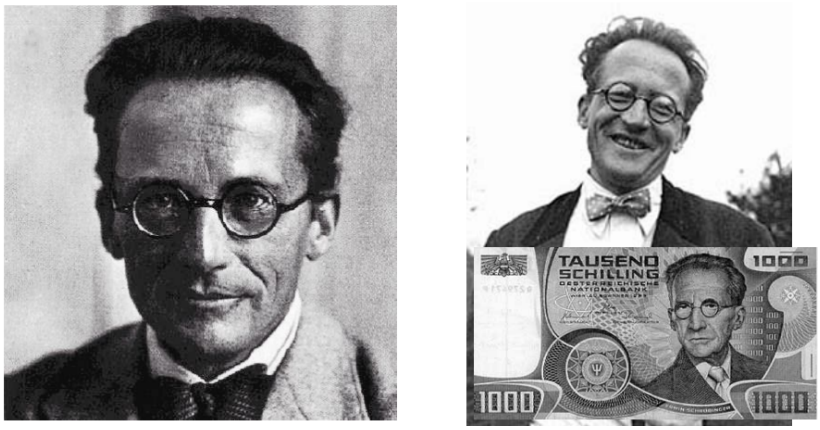


Figure 2.1:

In quantum mechanics the right hand side of the Schrödinger equation is written shortly as $\hat{H}\Psi(x,t)$, so (2.2) can be written as

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t}=\hat{H}\Psi(x,t) \quad (2.3)$$

This notation has a deeper reason, which is explained here shortly. The operation $-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x)\Psi(x,t)$ can be considered as a transformation of the function $\Psi(x,t)$, and the result is a another function of *x* and *t*. This means that the right hand side is a (specific) mapping from the set of functions to give again a function. The mapping is linear, and

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x) \quad (2.4)$$

is a linear transformation or **linear operator**, as it is called in quantum mechanics. The operator in question $\hat{H}$ is called the operator of the energy, that bears the name the **Hamilton operator** or the **Hamiltonian** for short. Later on, besides $\hat{H}$ we shall

encounter other types of linear operators, corresponding to physical quantities other than the energy. The form (2.4) of the Hamiltonian is used for the specific problem of a particle moving in one dimension *x*, where the external force field given by the potential energy function $V(x)$. For other problems the expression of the Hamiltonian is different, but the dynamical equation in the form (2.3) is the same. This is like in classical mechanics where the equation of motion for one particle is always $\dot{\mathbf{p}} = \mathbf{F}$ but $\mathbf{F}$, the force depends on the physical situation in question. In quantum mechanics the Schrödinger equation replaces Newton's equation of motion of classical mechanics which shows its fundamental significance.

We enumerate here a few important properties of the equation (2.2), or equivalently those of eq. (2.3):

- It is a linear equation, which means that if $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are solutions of the equation, then linear combinations of the form $c_1\Psi_1 + c_2\Psi_2$ will be also a solution, where c_1 and c_2 are complex constants. The summation can be extended to infinite sums, (with certain mathematical restrictions). Linearity is valid, because on both sides of the equation we have linear operations, derivations and multiplication with the given function $V(x)$.
- Another important property is that the equation is of first order in time. Therefore if we give an initial function at $t = t_0$ depending only on *x*: $\Psi(x,t_0) \equiv \psi_0(x)$, then by solving the equation we can find – in principle – a **unique** solution that satisfies this initial condition. There are of course infinitely many possible solutions, but they correspond to different initial conditions. The time dependence of the wave function from a given initial condition is called time evolution.
- The equation conserves the norm of the wave function, which means that if $\Psi(x,t)$ obeys (2.2), then the integral of the position probability density with respect to *x* is constant independently of *t*. Specifically, if this integral is equal to 1 at t_0, then it remains so for all times.

$$\int_{-\infty}^{\infty} |\psi_0(x)|^2 dx = 1 \Longrightarrow \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1, \quad \forall t \quad (2.5)$$

In other words the normalization property remains valid for all times. This property is called unitarity of the time evolution. The proof of this statement is left as a problem.

Problem 2.1

Using (2.2) prove that the time derivative of the normalization condition is zero, which means the validity of (2.5).

Stationary states

Specific solutions of eq. (2.2) can be found by making the **"ansatz"** (this German word used also in English math texts, and means educated guess), that the solution is a product of two functions

$$\Psi(x,t) = au(t)u(x) \quad (2.6)$$

where $au(t)$ depends only on time, while $u(x)$ is a space dependent function. This procedure is called separation. Not all the solutions of Eq. (2.2) have this separated form, but it is useful to find first these kind of solutions. Substituting back the product (2.6) into (2.2), we find

$$i\hbar u(x)\frac{\partial au(t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2} + V(x)u(x)\right) au(t) \quad (2.7)$$

Dividing by $au(t)u(x)$, we get:

$$i\hbar\frac{1}{au(t)}\frac{\partial au(t)}{\partial t} = \frac{1}{u(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2} + V(x)u(x)\right) \quad (2.8)$$

As the function on the left hand side depends only on time, while the one on the right hand side depends only on xx, and they must be equal for all values of these variables, this is possible only if both sides are equal to a constant independent of *x* and *t*. It is easy to check that the constant has to be of dimension of energy, and will be denoted by ε. We get then two equations. One of them is

$$i\hbar\frac{\partial au(t)}{\partial t} = au(t)\varepsilon \quad (2.9)$$

with the solution

$$au(t) = Ce^{-i\varepsilon t/\hbar} \quad (2.10)$$

where *C* is an integration constant.

The other equation takes the form:

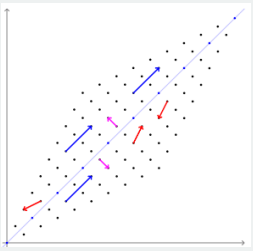
$$-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2}+V(x)u(x)=\varepsilon u(x) \quad (2.11)$$

We recognize that on the left hand side we have now again the operator $\hat{H}$ acting this time on $u(x)$:

$$\hat{H}u(x)=\varepsilon u(x) \quad (2.12)$$

This is a so called **eigenvalue problem**: the effect of the operator is such that it gives back the function itself multiplied by a constant. As the operator here is the Hamiltonian, i.e. the energy operator, (2.12) is an **energy eigenvalue equation**. Sometimes it is also called the (time independent) Schrödinger equation, but we shall not use this terminology.

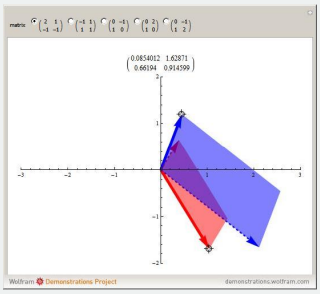
Animation



This simple gif animation tries to visualize the concepts of eigenvectors.

http://upload.wikimedia.org/Wikipedia/commons/0/06/Eigenvectors.gif

Animation



Drag each vector until the coloured parallelogram vanishes. If you can do this for two independent vectors, they form a basis of eigenvectors and the matrix of the linear map becomes diagonal, that is, nondiagonal terms are zero. This is impossible for some of the initial matrices—try them all. When you have found an eigenvector, check that it can be prolonged in its own direction while remaining an eigenvector; it is interesting to keep an eye on the matrix at the same time.

http://demonstrations.wolfram.com/EigenvectorsByHand/

It is important to stress here that Eq. (2.11) must be considered together with certain **boundary conditions** to be satisfied by the solutions $u(x)$ at the boundaries of their domain. In other words the boundary conditions are parts of the notion of the differential operator $\hat{H}$ in (2.11). The boundary conditions can be chosen in several different ways, and in general, physical considerations are used to choose the appropriate ones. In other words among the solutions of (2.11) one has to select those special ones where $u(x)$ obeys the boundary conditions which is usually possible only for certain specific values of ε. The functions $u_\varepsilon(x)$ obeying the equation with the given boundary conditions are called the **eigenfunctions** of $\hat{H}$ belonging to the corresponding energy eigenvalue ε: $\hat{H}u_\varepsilon(x)=\varepsilon u_\varepsilon(x)$.

According to the separation condition all the functions of the form

$$\psi_\varepsilon(x,t)=u_\varepsilon(x)e^{-i\varepsilon t/\hbar} \quad (2.13)$$

will be the solutions of the Schrödinger equation (2.2). The allowed energy eigenvalues εε, selected by the boundary conditions can be discrete, then they are usually labeled by integers $\varepsilon_n(n=1,2,\cdots)$, but they can also be continuous. In the latter case one finds

proper solutions for all ε-s within a certain energy interval. It can be easily shown that the physically acceptable solutions **must belong to real energy eigenvalues**.

Problem 2.2

Show that the normalization condition allows only real values of ε.

In general, there are infinitely many solutions of the form (2.13), but they do not exhaust all the solutions. As the Hamiltonian, as well as the Schrödinger-equation are linear, appropriate linear combinations of the specific solutions (2.13) also obey the Schrödinger equation, and have the general form:

$$\Psi(x,t) = \sum_n c_n u_n(x) e^{-i\varepsilon_n t/\hbar} + \int c(\varepsilon) u_\varepsilon(x) e^{-i\varepsilon t/\hbar} d\varepsilon \quad (2.14)$$

Here the complex numbers cncn and the complex function $c(\varepsilon)$ are arbitrary, the only condition is that the resulting $\Psi(x,t)$ must be normalizable, i.e. they must be such that the condition $\int |\Psi(x,t)|^2 dx = 1$ must hold.

It can also be shown – although this is usually far from simple – that for physically adequate potential energy functions, or $\hat{H}$ operators, all the solutions of (2.2) can be written in the form as given by (2.14).

The solutions $\psi_\varepsilon(x,t)$ of the form (2.13) are seen to be specific in the sense that they contain only a single term from the sum or integral in (2.14). Therefore the probability distributions corresponding to these solutions: $|\psi_\varepsilon(x,t)|^2 = |u_\varepsilon(x)|^2$ do not depend on time, while the wave functions i.e. the probability amplitudes are time dependent. These wave functions, and the corresponding physical states are called **stationary states**. According to (2.14) a general solution can be obtained by an expansion in terms of the stationary states.

The set of all eigenvalues is called the **spectrum** of the $\hat{H}$ operator, or the energy spectrum. Note that this terminology is different from the notion of the spectrum in experimental spectroscopy, but – as we will see – they are related to each other. In experimental spectroscopy an energy eigenvalue is called a **term**, and the spectrum seen e.g. in optical spectroscopy is the frequency corresponding to energy eigenvalue differences. The energy eigenfunctions belonging to given eigenvalues can be identified with the stationary states (orbits) postulated by Bohr. Therefore the existence of stationary states is the quantum mechanical proof of Bohr's first postulate. In addition QM also gives us the method how to find the energies and wave functions of the stationary states.

Now we shall introduce the following important property of the eigenfunctions of $\hat{H}$. It can be proven, that the integral of the product $u_n^*(x)u_{n'}(x)$ of eigenfunctions belonging to different eigenvalues $\varepsilon_n eq \varepsilon_{n'}$ vanishes $\int u_n^*(x)u_{n'}(x)dx = 0$, where the limits of the integration is taken over the domain of the eigenfunctions, usually between $-\infty$ and ∞. This property is called **orthogonality** of the eigenfunctions. If we also prescribe the normalization of the eigenfunctions, which can be always achieved by multiplying with an appropriate constant, we can write

$$\int u_n^*(x)u_{n'}(x)dx = \delta_{nn'} \quad (2.15)$$

where $\delta_{nn'}$ is Kronecker's symbol. Both orthogonality and normalization is taken together here, and we say therefore that the eigenfunctions are **orthonormal**.

There is a little more complicated but important point here. It may turn out, that one finds several **linearly independent solutions** of (2.11) with one and the same ε. Let the number of these solutions belonging to ε be g_ε. We say that ε is g_ε times **degenerate**. It can also be proven that among the degenerate solutions there are orthogonal ones whose number is g_ε. We can write this in the following way:

$$\int u_{nk}^*(x)u_{nk'}(x)dx = \delta_{kk'} \quad (2.16)$$

where $u_{nk}(x)$ means the k-th solution belonging to a given ε_n : $k = 1, 2 \ldots g_{\varepsilon_n}$.

Problem 2.3

Show that the probability density obtained from the linear combination of two stationary states belonging to different energy eigenvalues depends on time. What is the characteristic time dependence of this probability density?

An example: the linear harmonic oscillator

This is a very important system both in classical and in quantum physics, so besides demonstrating the way one solves quantum mechanical problems, it has far reaching applications in all branches of theoretical physics

The potential energy is $\frac{1}{2}Dx^2 = \frac{1}{2}m\omega^2 x^2$, and the eigenvalue equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 u(x) = \varepsilon u(x) \quad (2.17)$$

where $-\infty < x < \infty$

It will be useful to introduce the dimensionless coordinate ξ and the dimensionless energy ϵ by the relations:

$$\xi = \sqrt{m\omega/\hbar}x, \quad \epsilon = \frac{2\varepsilon}{\hbar\omega} \quad (2.18)$$

We obtain from (2.17)

$$\frac{\partial^2 u}{\partial \xi^2} + \left(\epsilon - \xi^2\right) u = 0 \quad (2.19)$$

We first find the asymptotic solution of this equation. For large values of $|\xi|$ we have $\frac{\partial^2 u}{\partial \xi^2} - \xi^2 u = 0$, with the **approximate** solution $e^{-\xi^2/2}$. (The term $\xi^2 e^{-\xi^2/2}$ will dominate over $e^{-\xi^2/2}$ for large $|\xi|$) The other possibility $e^{+\xi^2/2}$ must be omitted, because it is not square integrable, so it is not an allowed function to describe a quantum state.

The exact solutions of (2.19) are to be found in the form

$$u(\xi) = \mathcal{H}(\xi)e^{-\xi^2/2} \quad (2.20)$$

where $\mathcal{H}(\xi)$ is a polynomial of ξ. Substituting this assumption into 2.19, we get the equation

$$\frac{d^2\mathcal{H}}{d\xi^2} - 2\xi\frac{d\mathcal{H}}{d\xi} + (\epsilon - 1)\mathcal{H} = 0 \quad (2.21)$$

This is known as the differential equation for the Hermite polynomials. Looking for its solution as a power series $\mathcal{H} = \sum_k a_k \xi^k$, we find that the coefficients have to obey the recursion condition

$$(2k - \epsilon + 1)a_k = (k+2)(k+1)a_{k+2} \quad (2.22)$$

Problem 2.4

Derive (2.21) from the assumption (2.20) and (2.19). Derive the recursion formula, for the coefficients of the power series.

In case the series would be an infinite one, for large *k*-s we would have $a_{k+2} \simeq 2k a_k$, which is obtained by keeping only the highest order terms in *k* on both sides. This recursion relation is, however, the property of the series of e^{ξ^2} which would lead to a non square integrable function as the asymptotic form of *u* would then be again $e^{\xi^2}e^{-\xi^2/2} = e^{\xi^2/2}$. Therefore the sum determining $\mathcal{H}$ must remain finite, and so it **has to terminate at a certain integer power**, we shall denote it by ν. This means that all the coefficients higher than ν are zero, and in particular:

$$a_\nu eq 0, \quad a_{\nu+1} = 0, \quad a_{\nu+2} = 0 \quad (2.23)$$

In other words $\mathcal{H}$ is a polynomial of degree ν, and the condition $a_{\nu+1} = 0$ requires then that all the coefficients $0 = a_{\nu-1} = a_{\nu-3} = \ldots$ so the polynomials are either even or odd, depending on ν. In view of 2.23 we get 2.22 that $2\nu - \epsilon + 1 = 0$, or $\epsilon = 2\nu + 1$.

To summarize the result the eigenvalue equation has square integrable solutions only if

$$\varepsilon_\nu = \hbar\omega\left(\nu + \tfrac{1}{2}\right), \quad \nu = 0, 1, 2\ldots \quad (2.24)$$

where ν is called the vibrational quantum number. The possible energy values of the harmonic oscillator are equidistant with the separation $\Delta\varepsilon = \hbar\omega$. The lowest energy for $\nu = 0$, $\varepsilon_0 = \hbar\omega/2$ is not zero, but equals half of the level separation. ε_0 is called zero-point energy.

The corresponding eigenfunctions are

$$u_\nu(x) = \mathcal{N}_\nu \mathcal{H}_\nu\left(\sqrt{\tfrac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{\hbar}x^2/2} \quad (2.25)$$

where $\mathcal{H}_\nu$ -s are polynomials of degree ν, called Hermite polynomials, and $\mathcal{N}_\nu$-s are normalization coefficients. The square integrability is ensured by the exponential factor. For the highest nonvanishing coefficient of $\mathcal{H}_\nu$, which is not determined by the recursion, the convention is to set $a_\nu = 2^\nu$.

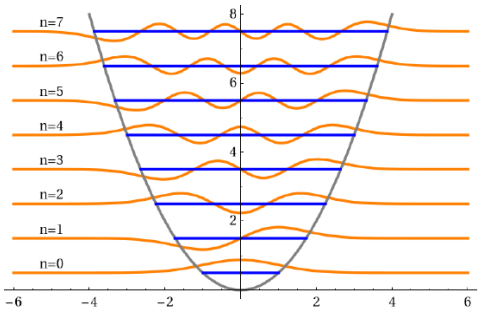


Figure 2.2: Energy eigenfunctions of the linear harmonic oscillator.

Problem 2.5

Determine the first 3 Hermite polynomials

It can be shown that the ϵ_ν eigenvalues are nondegenerate, so the eigenfunction $u_\nu(x)$ is unique (up to a constant factor). The eigenfunctions have also the important property of being orthonormal:

$$\int_{-\infty}^{\infty} u_{\nu'}(x) u_\nu(x) dx = \delta_{\nu'\nu} \quad (2.26)$$

The general time dependent solutions of the problem of the harmonic oscillator are of the form:

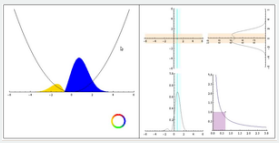
$$\Psi(x,t) = \sum_{\nu=0}^{\infty} c_\nu e^{-i\varepsilon_\nu t\hbar} u_\nu(x) = e^{-i\omega t/2} \sum_{\nu=0}^{\infty} c_\nu e^{-i\nu\omega t} u_\nu(x) \quad (2.27)$$

where the cvcv coefficients are complex constants, obeying the normalization condition $\sum_{\nu=0}^{\infty} |c_\nu|^2 = 1$. They are determined by the initial condition

$$\Psi(x,0) = \sum_{\nu=0}^{\infty} c_\nu u_\nu(x), \qquad \text{as lquad } c_\nu = \int_{-\infty}^{\infty} u_\nu(x)\Psi(x,0)dx \quad (2.28)$$

according to the orthonormality condition.

Animation

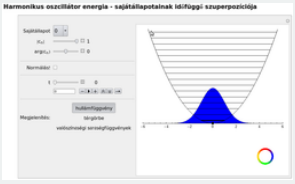


This animation shows the time evolution of the simple harmonic oscillator if it is initially in the superposition of the ground state $(n = 0)$ and the $n = 1$ state.

$\Psi(x,0) = \frac{1}{\sqrt{2}}(\varphi_0(x) + \varphi_1(x))$

http://titan.physx.u-szeged.hu/~mmquantum/videok/Harmonikus_oszcillator_szuperpozicio_0_1.flv

Animation



This interactive animation gives us a tool to play with the eigenfunctions of the linear harmonic oscillator. We can construct different linear combinations of the energy eigenfunctions and study their evolution in time.

http://titan.physx.u-szeged.hu/~mmquantum/download.php?download_file=HarmonikusOszcillatorIdofuggoSzuperpozicio.nbp

Expectation values and operators

The wave function gives the probability distribution of the position of a particle with the property (2.5). According to probability theory the expectation value or mean value of the position of the particle moving in one dimension is given by

$$\langle \hat{X} \rangle_\psi = \int_{-\infty}^{\infty} x|\psi(x)|^2 dx = \int \psi^*(x) x \psi(x) dx \quad (2.29)$$

the reason of writing capital $\hat{X}$ will be seen below. We did not put the limits deliberately in the second definite integral. In what follows, if the limits are not shown explicitly, then the integration always goes from $-\infty$ to $+\infty$, in one dimension, and over the whole three dimensional space in three dimensions. Therefore in an analogous way for a three-dimensional motion we can define the expectation value of the radius vector as

$$\langle \hat{\mathbf{R}} \rangle_\psi = \int \mathbf{r}|\psi(\mathbf{r})|^2 d^3\mathbf{r} = \int \psi^*(\mathbf{r}) \mathbf{r} \psi(\mathbf{r}) d^3\mathbf{r} \quad (2.30)$$

which actually means three different integrals for each component of $\mathbf{r}$. Now assume that the particle moves in an external force field given by the potential energy $V(\mathbf{r})$. If we know only the probability distribution and not the exact value of the particles position we cannot speak either about the value of the potential energy but only about its probability distribution. The expectation value of the potential energy is

$$\langle V(\hat{\mathbf{R}}) \rangle_\psi = \int \psi^*(\mathbf{r}) V(\mathbf{r}) \psi(\mathbf{r}) d^3\mathbf{r} \quad (2.31)$$

Note that the expectation value depends on the wave function, i. e on the physical state of the system, in which the quantities are measured. The general expectation value of a measurable quantity, $\hat{A}$ (which is called sometimes as an **observable**), is defined as,

$$\langle \hat{A} \rangle_\psi = \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d^3\mathbf{r} \quad (2.32)$$

where (\hat{A}\) is the **operator** corresponding to the physical quantity. An operator in the present context is an operation that transforms a square integrable function to another function. According to (2.29) the $\hat{X}$ operator corresponding to the coordinate multiplies the the wave function with the coordinate *x*.

$$\hat{X}\Psi(x,t) = x\Psi(x,t) \quad (2.33)$$

Or more generally in three dimensions:

$$\hat{\mathbf{R}}\Psi(\mathbf{r},t) = \mathbf{r}\Psi(\mathbf{r},t) \quad (2.34)$$

We may raise the question, what is the operator of the other fundamental quantity, momentum $\mathbf{p}$. It turns out that the corresponding operator is the derivative of ψ multiplied by the factor $\frac{\hbar}{i}$, or equivalently by $-i\hbar$:

$$\hat{P}_x\Psi(x,t) = -i\hbar\frac{\partial}{\partial x}\Psi(x,t) \quad (2.35)$$

$$\hat{\mathbf{P}}\Psi(\mathbf{r},t) = -i\hbar\nabla\Psi(\mathbf{r},t) \quad (2.36)$$

Then according to the general rule 2.32 we have in one dimension

$$\left\langle \hat{P}_x \right\rangle_\psi = -i\hbar \int \psi^*(x) \frac{\partial}{\partial x} \psi(x) dx \quad (2.37)$$

A justification of this statement is left to the next series of problems

Problem 2.6

Using the Schrödinger equation 2.2 prove that with the definitions above one has (in one dimension)

$$\left\langle \hat{P}_x \right\rangle_\psi = m\frac{d}{dt}\langle \hat{X} \rangle_\psi \quad (2.38)$$

Hints:

- Show that the time derivative of the expectation value of the coordinate can be calculated as

$$\frac{d}{dt}\langle \hat{X} \rangle = \frac{\hbar}{2im} \int \left(\frac{\partial^2 \Psi^*(x,t)}{\partial x^2} x\Psi(x,t) - \Psi^*(x,t) x \frac{\partial^2 \Psi(x,t)}{\partial x^2} \right) dx \quad (2.39)$$

- Rewrite the integrand as $\frac{\partial}{\partial x}\left(\frac{\partial \Psi}{\partial x}^{*} x \Psi - \Psi^{*} x \frac{\partial \Psi}{\partial x} - |\Psi|^{2}\right) + 2\Psi^{*}\frac{\partial \Psi}{\partial x}$, and assuming that $\Psi(x,t)$ goes to zero at $\pm\infty$ argue that only the last term contributes to the result.

Problem 2.7

Show that the expectation value of $\langle \hat{P} \rangle$ is real.

Problem 2.8

An operator $\hat{A}$ is called a self-adjoint or (Hermitian) if the following property holds for square integrable functions $\varphi(\mathbf{r})$ and $\psi(\mathbf{r})$

$$\int \varphi^{*}(\mathbf{r})[\hat{A}\psi(\mathbf{r})]d^{3}\mathbf{r} = \int [\hat{A}\varphi(\mathbf{r})]^{*}\psi(\mathbf{r})d^{3}\mathbf{r} \quad (2.40)$$

Show that the components of $\hat{\mathbf{R}}$ and $\hat{\mathbf{P}}$ are selfadjoint.

Problem 2.9

Show that the expectation value of a selfadjoint operator is real.

Noncommutativity of $\hat{X}$ and $\hat{P}$ operators

The fact that in quantum mechanics the coordinate and momentum are represented by operators – and they have the form we have given above – implies that their action on a wave function $\Psi(\mathbf{r},t)$ will give different result if they act on it in a different order:

$$\hat{X}\hat{P}_{x}\Psi(\mathbf{r},t) - \hat{P}_{x}\hat{X}\Psi(\mathbf{r},t) = -i\hbar x\frac{\partial}{\partial x}\Psi(\mathbf{r},t) + i\hbar\frac{\partial}{\partial x}[x\Psi(\mathbf{r},t)] = i\hbar\Psi(\mathbf{r},t) \quad (2.41)$$

or written in another way:

$$(\hat{X}\hat{P} - \hat{P}\hat{X})\Psi(\mathbf{r},t) = i\hbar\Psi(\mathbf{r},t) \quad (2.42)$$

for **any** function. This means that the action of the two operators are different, if they are taken in the reverse order, so this pair of operators is **noncommutative**. It is easily seen, that the same is true for Y and $\hat{P}_{y}$ and for $\hat{Z}$ and $\hat{P}_{z}$, while say $\hat{X}$ and $\hat{P}_{y}$ do commute, because the partial derivation by *y* gives zero for *x*. Similarly the components of $\hat{\mathbf{R}}$ among themselves as well as the components of $\hat{\mathbf{P}}$ among themselves commute with each other. Introducing the notation

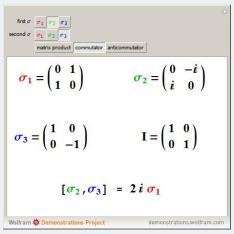
$$\hat{X}\hat{P}_{x} - \hat{P}_{x}\hat{X} =: \left[\hat{X}, \hat{P}_{x}\right] \quad (2.43)$$

which is called the **commutator** of the operators $\hat{X}$ and $\hat{P}_{x}$, we see that the commutator vanishes if the operators commute, and it is nonzero if this is not the case. To summarize we write down here the following **canonical commutation relations**:

$$\left[\hat{X}_{i}, \hat{X}_{j}\right] = 0, \quad \left[\hat{P}_{i}, \hat{P}_{j}\right] = 0, \quad \left[\hat{X}_{i}, \hat{P}_{j}\right] = i\hbar\delta_{ij} \quad (2.44)$$

From the operators of the coordinate and the momentum we can build up other operators depending on these quantities. The rule is that in the classical expression of a function of $\mathbf{r}$ and $\mathbf{p}$ we replace them by the corresponding operators. We will see for instance that the operator of orbital angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{R}} \times \hat{\mathbf{P}} = -i\hbar\mathbf{r} \times \nabla$, and the operator of energy in a conservative system is $\hat{H} = \frac{\hat{\mathbf{p}}^{2}}{2m} + V(\hat{\mathbf{R}}) = -\frac{\hbar^{2}}{2m}\Delta + V(r)$ in agreement with the definition given in (2.4)

Animation


matrix product
commutator
anticommutator
$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$\sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$
$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\mathrm{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$[\sigma_2, \sigma_3] = 2i\sigma_1$

Non commutativity arise also in case of matrix multiplication. This demonstration shows non commutativity in case of special 2×22×2 complex matrices, the so called Pauli matrices.

http://demonstrations.wolfram.com/PauliSpinMatrices/

Variance of an operator

There is an important number characterising a probability distribution, which is the property showing how sharp the distribution is. A measure of this property can be obtained, if we take the measured values of the random variable in question, and consider a mean value of certain differences between the measured values and the expectation value. As an example we consider again the one dimensional coordinate *x*. Taking the expectation value of the simple differences between the measured values and the expectation yields no information, as this gives zero in cases of all possible distributions due to the identity: $\int_{-\infty}^{\infty}\left[x'-\int_{-\infty}^{\infty}x|\psi(x)|^2dx\right]|\psi(x')|^2dx'=0$. A good measure is therefore to take the expectation value of the **square** of the differences from the expectation value, i.e. the quantity:

$$(\Delta\hat{X})_\psi^2:=\int_{-\infty}^{\infty}\left[x'-\int_{-\infty}^{\infty}x|\psi(x)|^2dx\right]^2|\psi(x')|^2dx' \quad (2.45)$$

which is called the **variance** of *x*, and which is the usual definition in probability theory, with a probability density $|\psi(x)|^2=\rho(x)$. We shall also call this the variance of the operator $\hat{X}$ in the state ψ. The latter terminology is due to the reformulation of the above definition as:

$$(\Delta\hat{X})_\psi^2=\left\langle\left(\hat{X}-\langle\hat{X}\rangle_\psi\right)^2\right\rangle_\psi \quad (2.46)$$

or in general for any linear and selfadjoint operator (2.32).

$$(\Delta\hat{A})_\psi^2=\left\langle\left(\hat{A}-\langle\hat{A}\rangle_\psi\right)^2\right\rangle_\psi \quad (2.47)$$

The variance is also called the second central moment of the probability distribution. The square root $\sqrt{(\Delta\hat{A})_\psi^2}=:(\Delta\hat{A})_\psi$ is called the **root mean square deviation** of the physical quantity $\hat{A}$ in the state given by ψ. We can rewrite this formula in two different ways. First it is simply seen that

$$(\Delta\hat{A})_\psi^2=\left\langle\hat{A}^2-2\hat{A}\langle\hat{A}\rangle_\psi+\langle\hat{A}\rangle_\psi^2\right\rangle_\psi=\left\langle\hat{A}^2\right\rangle_\psi-\langle\hat{A}\rangle_\psi^2 \quad (2.48)$$

because \(\langle\hat{A}\rangle_{\psi}/) is already a number. An important statement follows if we write

$$\begin{aligned}(\Delta\hat{A})_\psi^2&=\left\langle\left(\hat{A}-\langle\hat{A}\rangle_\psi\right)^2\right\rangle_\psi=\int\psi^*(\mathbf{r})\left(\hat{A}-\langle\hat{A}\rangle_\psi\right)^2\psi(\mathbf{r})d^3\mathbf{r}=\\&=\int\left[\left(\hat{A}-\langle\hat{A}\rangle_\psi\right)\psi(\mathbf{r})\right]^*\left[\left(\hat{A}-\langle\hat{A}\rangle_\psi\right)\psi(\mathbf{r})\right]d^3\mathbf{r}=\int|\hat{A}-\langle\hat{A}\rangle_\psi\psi(\mathbf{r})\Big)|^2d^3\mathbf{r}\end{aligned} \quad (2.49)$$

Based on this formula, we can simply answer the question: what kind of wave functions are those, where we can measure the quantity corresponding to $\hat{A}$ with zero variance, i.e. with a value which is always the same? In order to have $(\Delta\hat{A})_\psi^2=0$ the integral in the last expression must be zero. But as it is an integral of a squared absolute value being nonnegative everywhere, it can be zero if and only if $\left(\hat{A}-\langle\hat{A}\rangle_\psi\right)\psi(\mathbf{r})=0$, or stated otherwise, if and only if

$$\hat{A}\psi(\mathbf{r})=\langle\hat{A}\rangle_\psi\psi(\mathbf{r}) \quad (2.50)$$

Any function obeying this equation is called the eigenfunction of the operator $\hat{A}$. In the form above this equation has only a principal significance and in most cases knowing the operator, the eigenfunctions are not known a priori. Therefore the problem is usually to determine the eigenvalues and the eigenfunctions of $\hat{A}$ from the equation:

$$\hat{A}\varphi(\mathbf{r})=\alpha\varphi(\mathbf{r}) \quad (2.51)$$

This was the case above, in particular, for the Hamilton operator in (2.12).

Problem 2.10

Show that the expectation value of $\hat{A}$ in the state given by the normalized $\varphi(r)$, is just α.

An important theorem shows that the product of variances of two noncommuting operators has a lower bound, which is generally positive. In the case of the coordinate and momentum operators it takes the form

$$(\Delta\hat{X})_\psi \cdot \left(\Delta\hat{P}_x\right)_\psi \geq \frac{\hbar}{2} \quad (2.52)$$

for any wave function ψ, and a similar inequality holds for the other two (y, z) components. The mathematical proof of the inequality, which is called customarily as Heisenberg's uncertainty relation, will not be given here

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3: Angular momentum in quantum mechanics

Objectives

In this chapter we discuss the angular momentum operator – one of several related operators – analogous to classical angular momentum. The angular momentum operator plays a central role in the theory of atomic physics and other quantum problems involving rotational symmetry. In both classical and quantum mechanical systems, angular momentum (together with linear momentum and energy) is one of the three fundamental properties of motion.

Prerequisites

Chapters 1 and 2. Angular momentum and its conservation in classical mechanics. Spherical coordinates, elements of vector analysis. Laplace equation.

Eigenvalue equation in polar coordinates

The classical definition of the angular momentum vector is

$$\mathcal{L} = \mathbf{r} \times \mathbf{p} \quad (3.1)$$

which depends on the choice of the point of origin where |**r**|=r=0|r|=r=0. With the definition of the position and the momentum operators we obtain the angular momentum operator as

$$\hat{\mathbf{L}} = -i\hbar(\mathbf{r} \times \nabla) \quad (3.2)$$

The Cartesian components of $\hat{\mathbf{L}}$ are then

$$\hat{L}_x = -i\hbar\left(y\partial_z - z\partial_y\right), \quad \hat{L}_y = -i\hbar\left(z\partial_x - x\partial_z\right), \quad \hat{L}_z = -i\hbar\left(x\partial_y - y\partial_x\right) \quad (3.3)$$

One frequently needs the components of $\hat{\mathbf{L}}$ in spherical coordinates. In order to obtain them we have to make use of the expression of the position vector by spherical coordinates, which are connected to the Cartesian components by

$$\mathbf{r} = x\hat{\mathbf{e}}_x + y\hat{\mathbf{e}}_y + z\hat{\mathbf{e}}_z = r\sin\theta\cos\phi\hat{\mathbf{e}}_x + r\sin\theta\sin\phi\hat{\mathbf{e}}_y + r\cos\theta\hat{\mathbf{e}}_z \quad (3.4)$$

Going over to the spherical components in (3.3), and using the chain rule:

$$\partial_x = \left(\partial_x r\right)\partial_r + \left(\partial_x\theta\right)\partial_\theta + \left(\partial_x\phi\right)\partial_\phi \quad (3.5)$$

and similarly for ∂y and ∂z gives the following components

$$\begin{aligned}\hat{L}_x &= i\hbar\left(\sin\phi\partial_\theta + \cot\theta\cos\phi\partial_\phi\right)\\ \hat{L}_y &= i\hbar\left(-\cos\phi\partial_\theta + \cot\theta\sin\phi\partial_\phi\right)\\ \hat{L}_z &= -i\hbar\partial_\phi\end{aligned} \quad (3.6)$$

One sees at once the reason and the advantage of using spherical coordinates: the operators in question do not depend on the radial variable *r*. This is of course also true for $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ which turns out to be $-\hbar^2$ times the angular part of the Laplace operator $\Delta_{\theta\phi}$.

$$\hat{L}^2 = -\hbar^2\left(\partial_{\theta\theta}^2 + \cot\theta\partial_\theta + \frac{1}{\sin^2\theta}\partial_{\phi\phi}^2\right) = -\hbar^2\Delta_{\theta\phi} \quad (3.7)$$

We shall now find the eigenfunctions of $\Delta_{\theta\phi}$, that play a very important role in quantum mechanics, and actually in several branches of theoretical physics. They will be functions of $0 \le \theta \le \pi$ and $0 \le \phi < 2\pi$, i.e. they can be considered as complex valued functions whose domain is the unit sphere. The eigenfunctions of $\hat{L}^2$ will be denoted by $Y(\theta,\phi)$, and the angular eigenvalue equation is:

$$\begin{aligned}-\Delta_{\theta\phi}Y(\theta,\phi) &= \ell(\ell+1)Y(\theta,\phi) \quad \text{or}\\ \left(\partial_{\theta\theta}^2 + \cot\theta\partial_\theta + \frac{1}{\sin^2\theta}\partial_{\phi\phi}^2\right)Y(\theta,\phi) &= -\ell(\ell+1)Y(\theta,\phi)\end{aligned} \quad (3.8)$$

One might wonder what is the reason for writing the eigenvalue in the form $\ell(\ell+1)$, but as it will turn out soon, there is no loss of generality in this notation.

Separation of the eigenvalue equation

We try the separation of the variables:

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \quad (3.9)$$

Plugging this into (3.8) and dividing by $\Theta\Phi$, we find

$$\left\{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+\ell(\ell+1)\sin^2\theta\right\}+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=0 \quad (3.10)$$

The first term depends only on θ while the last one is a function of only ϕ. In order to satisfy this equation for all values of θ and ϕ these terms must be separately equal to a constant with opposite signs. This constant is traditionally denoted by m^2 and $-m^2$ (note that this is not the mass) and we have two equations: one for Θ, and another for Φ. We consider the second one, and have:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2 \quad (3.11)$$

Two linearly independent solutions are

$$\Phi(\phi)=\begin{cases} e^{im\phi} \\ e^{-im\phi} \end{cases} \quad (3.12)$$

and any linear combinations of them. One can choose $e^{im\phi}$, and include the other one by allowing mm to be negative. As these are functions of points in real three dimensional space, the values of $\Phi(\phi)$ and $\Phi(\phi+2\pi)$ must be the same, as these values of the argument correspond to identical points in space. Then $e^{im(\phi+2\pi)}=e^{im\phi}$, and $e^{im2\pi}=1$ must hold. From this it follows that mm must be an integer

$$\Phi(\phi)=\frac{1}{\sqrt{2\pi}}e^{im\phi} \quad m=0,\pm1,\pm2\ldots \quad (3.15)$$

The integration constant $\frac{1}{\sqrt{2\pi}}$ has been chosen here so that already $\Phi(\phi)$ is normalized to unity when integrating with respect to ϕ from 0 to 2π.

The equation for Θ

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[\ell(\ell+1)\sin^2\theta-m^2\right]\Theta=0 \quad (3.16)$$

is more complicated. With $\cos\theta=z$ the solution is

$$P_\ell^m(z):=\left(1-z^2\right)^{|m|2}\left(\frac{d}{dz}\right)^{|m|}P_\ell(z) \quad (3.17)$$

where $P_\ell(z)$ is the ℓ-th **Legendre polynomial**, defined by the following formula, (called the Rodrigues formula):

$$P_\ell(z):=\frac{1}{2^\ell\ell!}\left(\frac{d}{dz}\right)^\ell\left(z^2-1\right)^\ell \quad (3.18)$$

The functions $P_\ell^m(z)$ are called associated Legendre functions.

Problem 3.1

Find the first three Legendre polynomials $P_0(z)$, $P_1(z)$ and $P_2(z)$.

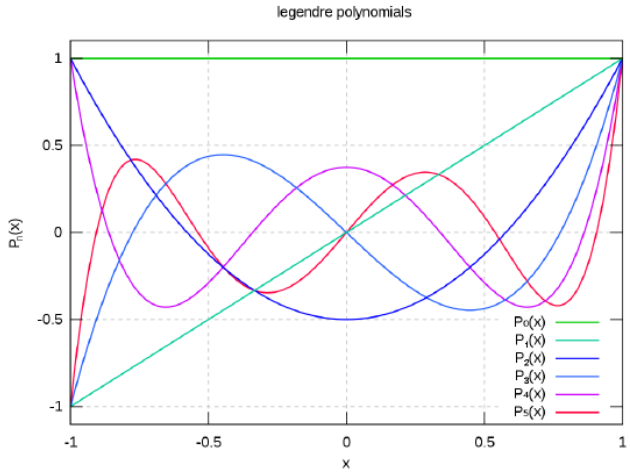


Figure 3.1: Plot of the first six Legendre polynomials.
http://en.Wikipedia.org/wiki/File:Legendrepolynomials6.svg

The function $P_\ell^m(z)$ is a polynomial in z only if $|m|$ is even, otherwise it contains a term $\left(1-z^2\right)^{|m|/2}$ which is a square root. But when turning back to $cos\theta = z$ this factor reduces to $(\sin\theta)^{|m|}$.

Problem 3.2

Find $P_2^0(\theta)$, $P_2^1(\theta)$, $P_2^2(\theta)$.

Problem 3.3

Prove that $P_\ell(z)$ are solutions of (3.16) for $m=0$.

Problem 3.4

Prove that $P_\ell^m(z)$ are solutions of (3.16) for all ℓ and $|m|$, if $|m| \le \ell$.

Problem 3.5

Show that $P_\ell(z)$ are either even, or odd depending on the parity of ℓ.

Notice that ℓ must be a nonnegative **integer** otherwise the definition (3.18) makes no sense, and in addition if |(|m|>ℓ\), then (3.17) yields zero. Thus for any given ℓ, there are $2\ell+1$ allowed values of m:

$$m = -\ell, -\ell+1, \ldots -1, 0, 1, \ldots \ell-1, \ell, \quad \text{for} \quad \ell = 0, 1, 2, \ldots \quad (3.19)$$

Note that equation (3.16) – as all second order differential equations – must have other linearly independent solutions different from $P_\ell^m(z)$ for a given value of ℓ and m. One can show however, that these latter solutions are divergent for $\theta = 0$ and $\theta = \pi$, and therefore they are not describing physical states. The solutions

$$Y_\ell^m(\theta,\phi) = \mathcal{N}_{lm} P_\ell^m(\theta) e^{im\phi} \quad (3.20)$$

where the absolute values of the constants $\mathcal{N}_{lm}$ ensure the normalization over the unit sphere, are called **spherical harmonics**. There are several different conventions for the phases of $\mathcal{N}_{lm}$, so one has to be careful with them.

The $Y_\ell^m(\theta)$ functions are thus the eigenfunctions of $\hat{L}$ corresponding to the eigenvalue $\hbar^2\ell(\ell+1)$, and they are also eigenfunctions of $\hat{L}_z = -i\hbar\partial_\phi$, because

$$\hat{L}_z Y_\ell^m(\theta,\phi) = -i\hbar\partial_\phi Y_\ell^m(\theta,\phi) = \hbar m Y_\ell^m(\theta,\phi) \quad (3.21)$$

The quantum number ℓ is called **angular momentum quantum number**, or sometimes for a historical reason as azimuthal quantum number, while m is the **magnetic quantum number**.

Concluding the subsection let us note the following important fact. As none of the components of $\hat{\mathbf{L}}$, and thus nor $\hat{L}^2$ depends on the radial distance rr from the origin, then any function of the form $\mathcal{R}(r)Y_\ell^m(\theta,\phi)$ will be the solution of the eigenvalue equation above, because from the point of view of the $\hat{\mathbf{L}}$ the $\mathcal{R}(r)$ function is a constant, and we can freely multiply both sides of (3.8). by $\mathcal{R}(r)$.

Orthonormality and completeness

The spherical harmonics form an infinite **system of orthonormal functions** in the sense:

$$\int_0^{2\pi}\int_0^{\pi}\left(Y_{\ell'}^{m'}(\theta,\phi)\right)^* Y_\ell^m(\theta,\phi)\sin\theta d\theta d\phi = \delta_{\ell\ell'}\delta_{mm'} \quad (3.22)$$

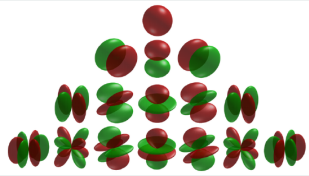
This system is also a **complete** one, which means that any complex valued function $g(\theta,\phi)$ that is square integrable on the unit sphere, i.e. $\int |g(\theta,\phi)|^2 \sin\theta d\theta d\phi < \infty$ can be expanded in terms of the $Y_\ell^m(\theta,\phi)$):

$$g(\theta,\phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m} Y_\ell^m(\theta,\phi) \quad (3.23)$$

where the expansion coefficients can be obtained similarly to the case of the complex Fourier expansion by

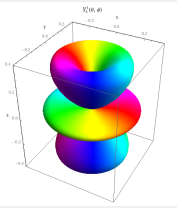
$$c_{\ell m} = \int_0^{2\pi}\int_0^{\pi}\left(Y_\ell^m(\theta,\phi)\right)^* g(\theta,\phi)\sin\theta d\theta d\phi \quad (3.24)$$

Further Reading



If you are interested in the topic Spherical harmonics in more details check out the Wikipedia link below:
http://en.Wikipedia.org/wiki/Spherical_harmonics

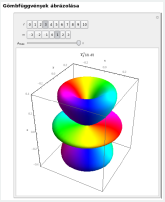
Animation



The animation shows the time dependence of the stationary state – i.e. the one containing the time dependent factor $e_{-i\epsilon t/\hbar}$ as well – given by the function $Y_1^3(\theta,\phi)$. The absolute value of the function in the direction given by θ and ϕ is equal to the distance of the point from the origin, and the argument of the complex number is obtained by the colours of the surface according to the phase code of the complex number in the chosen direction.

http://titan.physx.u-szeged.hu/~mmquantum/videok/Gombfuggveny_fazis_idofejlodes.flv

Animation



The figures show the three-dimensional polar diagrams of the spherical harmonics. The state to be shown, can be chosen by setting the quantum numbers ℓ and m.

http://titan.physx.u-szeged.hu/~mmquantum/interactive/Gombfuggvenyek.nbp

Specific examples

The first few functions are the following, with one of the usual phase (sign) conventions:

$$Y_0^0(\theta,\phi)=\frac{1}{\sqrt{4\pi}} \quad (3.25)$$

$$Y_1^0(\theta,\phi)=\sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_1^1(\theta,\phi)=-\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}, \quad Y_1^{-1}(\theta,\phi)=\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \quad (3.26)$$

Historically the spherical harmonics with the labels $\ell=0,1,2,3,4$ are called $s,p,d,f,g\ldots$ functions respectively, the terminology is coming from spectroscopy.

If an external magnetic field $\mathbf{B}=\{0,0,B\}$ is applied, the projection of the angular momentum onto the field direction is $\hbar m$. Since mm can take only the integer values between $-\ell$ and $+\ell$, there are $2\ell+1$ different possible projections, corresponding to the $2\ell+1$ different functions $Y_m^\ell(\theta,\phi)$ with a given ℓ.

Very often the spherical harmonics are given by Cartesian coordinates by exploiting $\sin\theta e^{\pm i\phi}=(x\pm iy)/r$ and $\cos\theta=z/r$. Another way of using these functions is to create linear combinations of functions with opposite m-s. This is useful for instance when we illustrate the orientation of chemical bonds in molecules. We demonstrate this with the example of the p functions.

$$\begin{aligned} p_x &= \frac{x}{r}=\frac{\left(Y_1^{-1}-Y_1^1\right)}{\sqrt{2}}=\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi \\ p_x &= \frac{y}{r}=-\frac{\left(Y_1^{-1}+Y_1^1\right)}{\sqrt{2}}=\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi \\ p_z &= \frac{z}{r}=Y_1^0=\sqrt{\frac{3}{4\pi}}\cos\theta \end{aligned} \quad (3.27)$$

Let us also note that the $m=0$ functions do not depend on ϕ, and they are proportional to the Legendre polynomials in $cos\theta$.

$$Y_\ell^0(\theta)=\sqrt{\tfrac{2\ell+1}{4\pi}}P_\ell(\cos\theta) \quad (3.28)$$

Parity and angular momentum

The operator of parity Π is defined in the following way:

$$\Pi\psi(\mathbf{r})=\psi(-\mathbf{r}) \quad (3.29)$$

The result of acting by the parity on a function is the mirror image of the original function with respect to the origin. Looking for the eigenvalues and eigenfunctions of Π, we note first that $\Pi^2=1$. Therefore the single eigenvalue of Π^2 is 1, and any function is its eigenfunction. The eigenvalues of Π itself are then ±1, and we have the following two possibilities:

$$\begin{aligned} \Pi_{\psi_+}(\mathbf{r}) &= \quad \psi_+(-\mathbf{r})=\psi_+(\mathbf{r}) \\ \Pi_{\psi_-}(\mathbf{r}) &= \quad \psi_-(-\mathbf{r})=-\psi_-(\mathbf{r}) \end{aligned} \quad (3.30)$$

In the first case the eigenfunctions $\psi_+(\mathbf{r})$ belonging to eigenvalue +1 are the even functions, while in the second we see that $\psi_-(\mathbf{r})$ are the odd functions belonging to the eigenvalue −1. There are of course functions which are neither even nor odd, they do not belong to the set of eigenfunctions of Π.

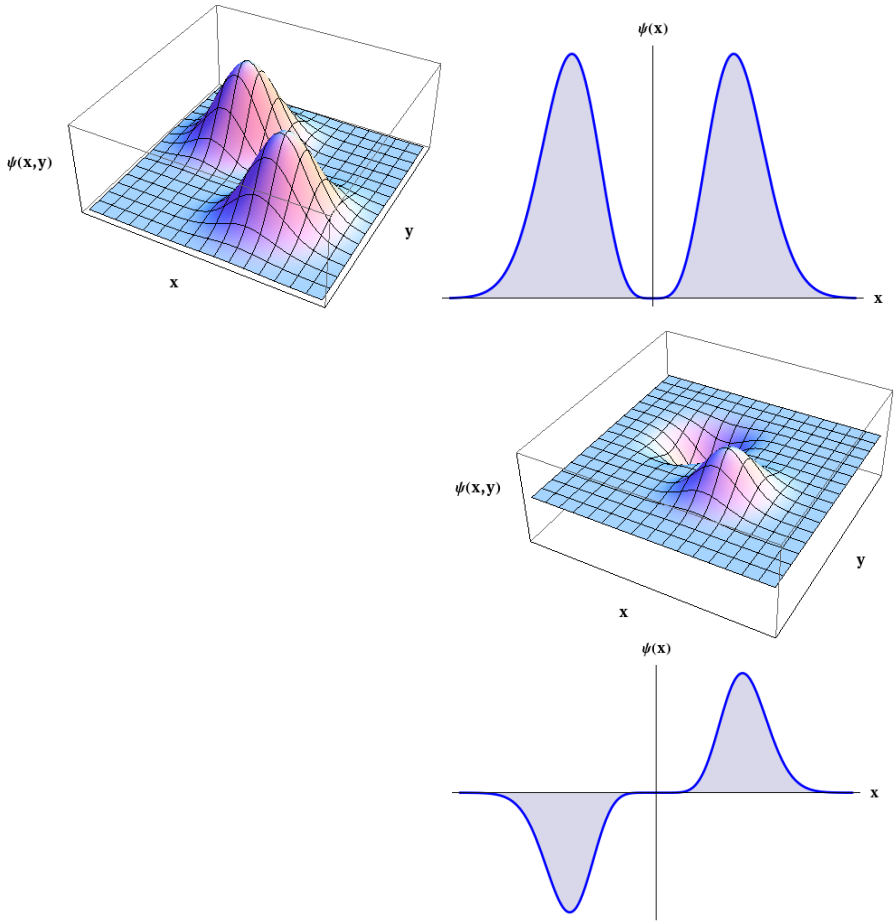


Figure 3.2: Examples of even and odd functions in one and two dimensions.

The reason why we consider parity in connection with the angular momentum is that the simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ the spherical harmonics times any function of the radial variable r are eigenfunctions of Π as well, and the corresponding eigenvalues are $(-1)^\ell$. This can be formulated as:

$$\Pi\mathcal{R}(r)Y_\ell^m(\theta,\phi) = \mathcal{R}(r)\Pi Y_\ell^m(\theta,\phi) = (-1)^\ell \mathcal{R}(r)Y(\theta,\phi) \quad (3.31)$$

Problem 3.6

Show that the transformation $\{x, y, z\} \longrightarrow \{-x, -y, -z\}$ is equivalent to $\theta \longrightarrow \pi - \theta, \quad \phi \longrightarrow \phi + \pi$.

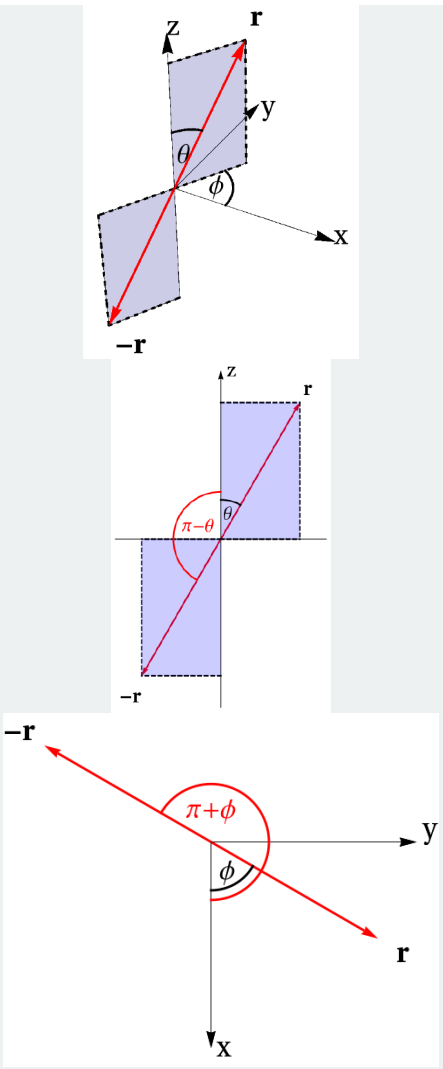


Figure 3.3: The effect of the transformation $\{x, y, z\} \longrightarrow \{-x, -y, -z\}$

Problem 3.7

By using the results of the previous subsections prove the validity of Eq. (3.31).

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4: Atomic spectra, simple models of atoms

Objectives

Quantum mechanics had initially the aim to explain the line spectra of atoms seen in optical spectroscopy. The first successful attempt was the Bohr model based on seemingly "ad hoc" postulates. These postulates are actually consequences of the elegant mathematical treatment of the Coulomb problem based on first principles of quantum mechanics. The appearance of angular momentum in this special case hints to its significance in quantum physics.

Prerequisites

The Kepler-Newton problem in classical mechanics, Chapter 3.

Bohr's postulates and the Bohr model

Quantum mechanics had initially the aim to explain the line spectra of atoms seen in optical spectroscopy. Later on it became a fundamental theory explaining all the microscopic phenomena including molecular-, solid state-, nuclear-, and high energy particle physics.

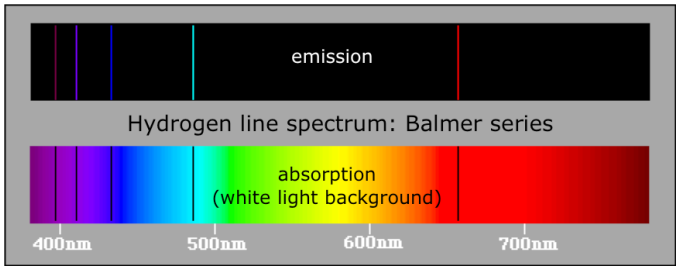


Figure 4.1: Emission and absorption spectra of the Balmer series of hydrogen.
http://www.goiit.com/posts/list/community-shelf-the-bohr-atom-917720.htm

Before going into some details of the quantum mechanical explanation, first we recall how Niels Bohr explained the spectra of atomic gases. He established two postulates.

- Among the classically allowed orbits of the electron moving around the nucleus, there are certain stationary orbits or stationary states with definite energy. The atoms do not radiate if the electron is on such a stationary orbit.
- Electrons can only gain and lose energy by jumping from one allowed orbit with energy E_1 to another, with E_2 absorbing or emitting electromagnetic radiation with a frequency ν determined by the energy difference of the levels according to the Planck relation:

$$\begin{aligned} \text{absorbtion}: h\nu &= E_2 - E_1 \qquad \text{if} \quad E_2 > E_1 \\ \text{emission}: \quad h\nu &= E_1 - E_2 \qquad \text{if} \quad E_1 > E_2 \end{aligned} \tag{4.1}$$

where *h* is Planck's constant.

These postulates cannot be understood on the basis of classical physics. An electron moving around the nucleus has a centripetal acceleration, and as all accelerating electric charges it is expected to radiate and lose energy. This would eventually let it fall into the nucleus, so the atom could not be a stable object, which is in sharp contradiction with observations. Therefore the postulates seemed to be "ad hoc". Still they were highly significant, because these statements turned out to be true in view of the "true" quantum mechanics, as well. In that theory, however, these are not fundamental statements but consequences of the deeper general principles and formalism of quantum mechanics.

In addition to these postulates Bohr set up a rule for the H atom how the discrete stationary energies can be obtained again by an ad hoc quantum condition. He prescribed that on these stationary orbits the angular momentum ℓ of the electron orbiting on a circle can have only discrete values, namely an integer multiple of $\hbar = h/2\pi$ the Planck constant divided by 2π:

$$\mathcal{L} = mvr = n\hbar, \quad n = 1, 2 \ldots \tag{4.2}$$

This is called Bohr's quantization condition. Combining this with the equation of motion of the electron:

$$\frac{q_0^2}{4\pi\epsilon_0}\frac{1}{r^2} = m\frac{v^2}{r} \quad (4.3)$$

i.e. (Coulomb) force equals to mass times (centripetal) acceleration, the total energy of the electron on the circular orbit, of radius r can be calculated from the expression,

$$E = \frac{mv^2}{2} - \frac{q_0^2}{4\pi\epsilon_0}\frac{1}{r} \quad (4.4)$$

where the first term is the kinetic energy while the second is the potential energy of the electron in the electric field of the point-like nucleus, one can derive two important results. Introducing the notations

$$e_0^2 = \frac{q_0^2}{4\pi\epsilon_0} \qquad a_0 = \frac{\hbar^2}{me_0^2} \quad (4.5)$$

first, the allowed energy values of the stationary states are obtained as

$$E_n = -\frac{me_0^4}{2\hbar^2}\frac{1}{n^2} = -\frac{e_0^2}{2a_0}\frac{1}{n^2} \qquad n = 1, 2\ldots \quad (4.6)$$

Second, the allowed values of the radii of the stationary orbits are:

$$r_n = a_0 n^2 \quad (4.7)$$

a_0 is called the first Bohr radius and its value is $a_0 = 0.053nm$, and

$$\begin{aligned} E_n &= E_1\frac{1}{n^2} \\ E_1 &= -2.2\text{aJ} = -13.6\text{eV} = -1\text{ Rydberg } = -1/2\text{hartree} \end{aligned} \quad (4.8)$$

The negative sign means that the electron is in a bound state, as the zero level of the potential energy is at $r = \infty$, where the electron becomes free and has zero energy if $\nu = 0$. The state with this lowest value of energy is called the ground state of the H atom, and $-E_1$ is the minimal energy to be given to a H atom in order to ionize it, i.e. to strip off the electron from the nucleus. These results were in accordance with the experimental observations of the emission line spectrum of atomic Hydrogen, the different series, etc. with the Rydberg formula (See Figure 4.2).

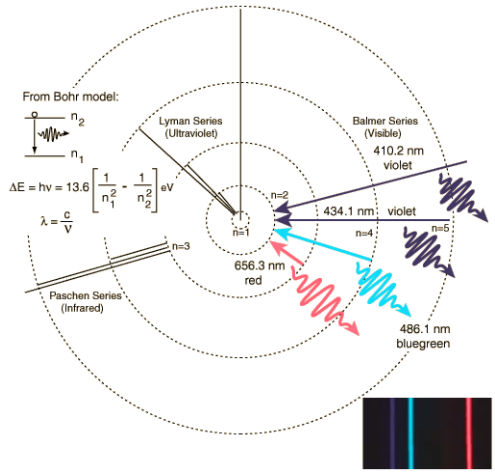


Figure 4.2: Visualization of the emission spectrum lines of atomic Hydrogen.
http://hyperphysics.phy-astr.gsu.edu/hbase/hyde.html

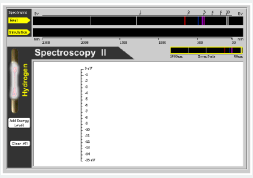
Problem 4.1

Calculate the wavelengths of the first four Balmer lines which correspond to transitions arriving to the level with $n = 2$. What is the limit of these lines where the continuum begins?

Be, as it is, funny, the results above did turn out to be true, although the premises we started from were definitely wrong. There is a quantization condition for the angular momentum given but in a very different sense than that given in the Bohr model. And this quantization condition is rather a result of the deeper principles of quantum mechanics – explained in section 2 – than an apriori assumption. So this accidental coincidence shows that starting from start premise one can arrive to any result, including the ce

correct one. Similar assumption did not lead however to reasonable results in the case of more complicated atoms, and had to be abandoned in the view of quantum mechanics.

Animation



We can investigate the origin of spectral lines in several steps with this interactive shockwave animation.

http://phys.educ.ksu.edu/vqm/free/h2spec.html

The radial equation of quantum mechanics

The Schrödinger energy eigenvalue equation for any central field problem, including in particular the Coulomb potential has the form

$$-\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r})+V(|\mathbf{r}|)\psi(\mathbf{r})=\varepsilon\psi(\mathbf{r}) \quad (4.9)$$

where the potential energy depends only on the value $|\mathbf{r}|=r$ i.e. on the distance from a centre.

We shall now outline the procedure how the energy eigenvalues and the stationary states can be obtained mathematically, restricting ourselves only to the bound states, that play a very important role in atomic physics, not only in the case of the H atom. In order to find the solution of this equation one introduces **spherical coordinates**, $\psi(\mathbf{r})=\psi(r,\theta,\phi)$ indicated by the spherical symmetry of the potential. The eigenvalue equation takes the form

$$-\frac{\hbar^2}{2m}\left(\Delta_r+\frac{1}{r^2}\Delta_{\theta\phi}\right)\psi(r,\theta,\varphi)+V(r)\psi(r,\theta,\varphi)=\varepsilon\psi(r,\theta,\phi) \quad (4.10)$$

where and $\Delta_{\theta\phi}$ are the radial and angular parts of the Laplacian, respectively. We separate the radial and angular parts of the wave function with the ansatz (assumption)

$$\psi(\mathbf{r})=\psi(r,\theta,\phi)=\mathcal{R}(r)Y_\ell^m(\theta,\phi)=\frac{u(r)}{r}Y_\ell^m(\theta,\phi) \quad (4.11)$$

Using the results of the previous section about angular momentum we obtain the following ordinary differential equation for $\mathcal{R}(r)$

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)\mathcal{R}(r)+\hbar^2\frac{1}{2m}\frac{\ell(\ell+1)}{r^2}\mathcal{R}(r)+V(r)\mathcal{R}(r)=\varepsilon\mathcal{R}(r) \quad (4.12)$$

This is called the **radial equation**, yielding

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}u(r)+V(r)u(r)=\varepsilon u(r) \quad (4.13)$$

for $u(r)=r\mathcal{R}(r)$ which is also called sometimes radial equation.

Problem 4.2

Show that $u(r)$ obeys the equation (4.13).

The latter form for the unknown $u(r)$ is similar to a one dimensional eigenvalue problem, containing an effective potential $V(r)+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$, where the last term is a centrifugal potential, appearing also in the corresponding classical problem in the form $\mathcal{L}^2/2mr^2$.

Asymptotic behaviour of the solutions

Asymptotics in infinity

As we assume that $V(\infty)\to 0$, then for $r\to\infty$ the potential energy and the centrifugal energy are negligible and we obtain the equation

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}=\varepsilon u \quad (4.14)$$

We rewrite it as

$$\frac{d^2u}{dr^2}+\frac{2m}{\hbar^2}\varepsilon u=0 \quad (4.15)$$

If , corresponding $\varepsilon \geq 0$, the two solutions are e^{ikr} and e^{-ikr}. As we noted earlier these are not square integrable. The corresponding $\mathcal{R}(r)$ behave as

$$\mathcal{R}_+(r)\sim \tfrac{1}{r}e^{i(kr-\varepsilon t)} \quad \mathcal{R}_-(r)\sim \tfrac{1}{r}e^{-i(kr+\varepsilon t)} \quad \text{for } r\to\infty \quad (4.16)$$

where time dependence was included in order to see, that $\mathcal{R}_+(r)$ describes an outgoing spherical wave, an electron with positive total energy that can leave the atom for $r\to\infty$. $\mathcal{R}_-(r)$ is an incoming spherical wave, and both are used for the description of scattering processes, which we do not analyze here.

Square integrable solutions are obtained only if $\varepsilon<0$. Then with the notation:

$$0<-\frac{2m}{\hbar^2}\varepsilon =: \kappa^2 \quad (4.17)$$

the two appropriate linearly independent solutions of Eq. (4.15) are $e^{\kappa r}$ and $e^{-\kappa r}$, the first of which is not square integrable on $[0,\infty)$ because $\kappa>0$. The second solution is proper, as it decays exponentially for $r\to\infty$, that is why it will lead to bound state, which is square integrable. Thus we have:

$$u(r\to\infty)\sim e^{-\kappa r} \quad (4.18)$$

Asymptotics near the origin

We assume here that the potential energy $V(r)$ remains finite at $r=0$, or even if it diverges that is not faster than $1/r^2$. The Coulomb potential belongs to this class, as it is divergent only as $1/r$. Then in the radial equation (4.13) the potential energy and εu can be omitted besides the dominant centrifugal term, getting to the second order equation

$$\frac{d^2u}{dr^2}-\frac{\ell(\ell+1)}{r^2}=0 \quad (4.19)$$

which has a two solutions $r^{\ell+1}$ and $1/r^{\ell}$.

Problem 4.3

Find the solutions of (4.19) in the form r^k.

Show that $1/r^{\ell}$ is not square integrable on $[0,\infty)$, if $\ell>0$

According to the solution of the problem above, the solution of the form of $1/r^{\ell}$ will not be an appropriate one if $\ell>0$, and by a little more subtle argumentation it can be shown that this holds true for $\ell=0$, as well. This means that we can afford only the nonsingular solution $r^{\ell+1}$ close to $r=0$, i.e. the radial part of the wave function around 0 behaves as.

$$\mathcal{R}(r)=u(r)/r\sim r^{\ell} \quad (4.20)$$

i.e it goes to zero if $\ell eq 0$, and remains constant for $\ell=0$, ie. for **s states**.

The radial equation for the bound states can be written with the notation introduced in (4.17)

$$\frac{d^2u}{dr^2}-\frac{\ell(\ell+1)}{r^2}u-\frac{2m}{\hbar^2}V(r)u=-\frac{2m}{\hbar^2}\varepsilon u=\kappa^2 u \quad (4.21)$$

It will be useful to write the equation in terms of dimensionless variable $\kappa r=\varrho$:

$$\left(\frac{d^2}{d\varrho^2}-\frac{\ell(\ell+1)}{\varrho^2}-\frac{V(\varrho/\kappa)}{|\varepsilon|}-1\right)u(\varrho)=0 \quad (4.22)$$

where the asymptotic conditions require $u(\varrho\to 0)\sim\varrho^{\ell+1}$ and $u(\varrho\to\infty)\sim e^{-\varrho}$.

This radial equation is often used in atomic physics, a solution in a closed analytic form can be obtained only if the potential $V(r)$ has certain special forms. Therefore one usually applies numerical methods for the solutions. For one of the most important cases: the $1/r$ Coulomb type potential the solutions can be expressed in terms of elementary analytic functions. The next section deals with this problem.

Eigenvalue problem of the Coulomb potential

In the case of the attractive Coulomb field the radial equation will be written for the more general case of Hydrogen-like ions, where the number of protons in the nucleus is $Z \geq 1$, which bound a single electron. Examples are the singly ionized Helium: $He^{+}(Z=2)$, doubly ionized Lithium $Li^{++}(Z=3)$, etc. The potential energy is then $V(r) = -\frac{Ze_0^2}{r}$, where the notation of Eq. (4.5) is used. With $\kappa r = \varrho$, $V(\varrho/\kappa) = -\frac{Ze_0^2\kappa}{\varrho}$, and the third term in the radial equation is $\frac{V(\varrho/\kappa)}{|\varepsilon|} = -\frac{2mZe_0^2}{\hbar^2\kappa}\frac{1}{\varrho} = -\frac{\varrho_0}{\varrho}$. where we have introduced the notation:

$$\varrho_0 = \frac{2mZe_0^2}{\hbar^2\kappa} = \frac{2Z}{\kappa a_0} \quad (4.1)$$

The radial equation itself takes the form:

$$\left(\frac{d^2}{d\varrho^2} - \frac{\ell(\ell+1)}{\varrho^2} + \frac{\varrho_0}{\varrho} - 1\right) u(\varrho) = 0 \quad (4.2)$$

According to the asymptotic conditions obtained in the previous subsection we seek the solution as

$$u(\varrho) = \varrho^{\ell+1} w(\varrho) e^{-\varrho} \quad (4.3)$$

where the factor $\varrho^{\ell+1}$ takes care about the proper behaviour close to zero, the factor $e^{-\varrho}$ at infinity, and $w(\varrho)$ – which is to be determined – should ensure that this form of $u(\varrho)$ is the exact solution of equation (4.2). Putting the expression of uu given by (4.3) into (4.2), we obtain the differential equation:

$$\varrho\frac{d^2w}{d\varrho^2} + 2(\ell+1-\varrho)\frac{dw}{d\varrho} + (\varrho_0 - 2(\ell+1))\, w = 0 \quad (4.4)$$

The solution of the equation for $w(\varrho)$ must not vitiate the prescribed asymptotic forms stipulated by (4.3), which means that $w(\varrho)$ must have a power series (with positive exponents) around zero, and for $\varrho \to \infty$ it must grow slower than e^{ϱ} in order to maintain the condition $u(\varrho \to \infty) \sim e^{-\varrho}$ If one looks for a solution

$$w(\varrho) = \sum_{k=0}^{\infty} a_k \varrho^k \quad (4.5)$$

and substitutes it into (4.4), one obtains a recurrence relation between the coefficients :

$$a_{k+1} = \frac{2(k+\ell+1)-\varrho_0}{(k+1)(k+2\ell+2)} a_k \quad (4.6)$$

In addition it can be shown that if the series (4.5) were infinite, the recurrence relation would behave as the one of the power series of $e^{2\varrho}$ which would mean that the asymptotic condition $u(\varrho \to \infty) \sim e^{-\varrho}$ would be replaced by $u(\varrho \to \infty) \sim e^{\varrho}$ which was not allowed, as we required square integrability. Therefore the sum in (4.5) must remain finite. This means that there exist an integer n_r, for which $a_{n_r} eq 0$, but $a_{n_r+1} = 0$, and then, as it follows from (4.6), all $a_k = 0$, for $k > n_r$. In other words the sum giving $w(\varrho)$ must reduce to a polynomial of degree n_r. This is possible, if and only if the nominator of the coefficient of a_{n_r} given by the right hand side of of (4.6) vanishes, thus:

$$\varrho_0 = 2\,(n_r + \ell + 1) \quad (4.7)$$

The degree n_r of the polynomial *w* is called as **radial quantum number**. Now one introduces the **principal quantum number** with the definition

$$n := n_r + \ell + 1 \quad (4.8)$$

which is a positive integer. The name principal is given to it, because this is the quantum number that determines the energy eigenvalues. (This statement will be refined later). In order to see this we recall the notation introduced in (4.1)

$$\varrho_0 = \frac{2mZe_0^2}{\hbar^2\kappa} = \frac{2Z}{\kappa a_0} = 2n \quad (4.9)$$

and we get $\kappa_n = \frac{Z}{na_0} = \frac{2mZe_0^2}{\hbar^2 n}$. From the definition of κ, namely $\varepsilon = -\frac{\hbar^2\kappa^2}{2m}$ the eigenvalues corresponding to the Coulomb potential are the following:

$$\varepsilon_n = -\frac{mZ^2e_0^4}{2\hbar^2}\frac{1}{n^2} = -Z\frac{e_0^2}{2a_0}\frac{1}{n^2}, \quad n = 1, 2\ldots \quad (4.10)$$

This is the most important result: it turns out that the energy eigenvalue equation has **square integrable** solutions only if $\varepsilon < 0$, and in addition only if ε equals to certain discrete numbers, which are equal to those obtained by Bohr from his (erroneous) quantization condition.

The energy eigenvalues of this **discrete spectrum** are called the **bound state energies** of the Coulomb potential.

The eigenvalues agree very well with the experimental values of the primary spectrum of the H atom $(Z = 1)$ the Lyman, Balmer etc. series. The result also agrees with the formula obtained from the Bohr model. But the Bohr model works only for the H atom, i.e. for the Coulomb potential, while the quantum mechanical procedure works well with any potential.

With the procedure above, we obtained the discrete spectrum, where the role of the boundary conditions is to be remembered. It is important, however, that there are also solutions with $\varepsilon > 0$, where ε can be any nonnegative number. The latter part of the eigenvalues form the **continuous spectrum**, and the corresponding eigenstates are the **scattering states**. These functions are not square integrable, but similarly to the the De Broglie waves, continuous superpositions can be formed from them which are in turn square integrable.

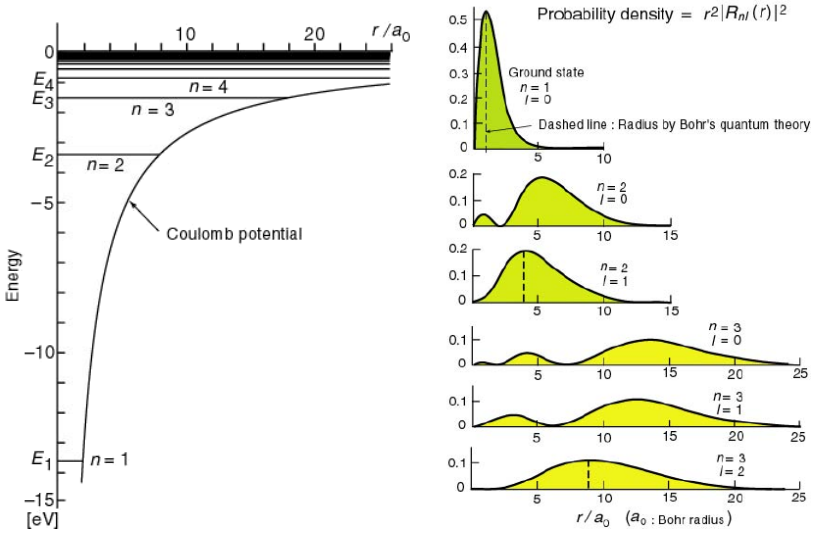
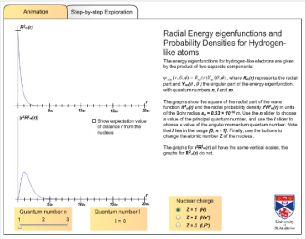


Figure 4.3: On the left you can see the energy diagram of the stationary states of the Hydrogen atom. While on the right figures show the position probability densities of the electron-nucleus densities in the states $\left(r^2|\mathcal{R}_{n\ell}(r)|^2\right)$.

http://www.kutl.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm

Animation



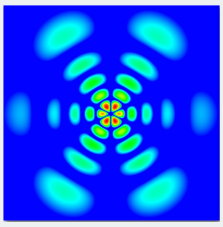
With this flash animation you can investigate the radial eigenfunctions and probability densities $\left(r^2|\mathcal{R}_{n\ell}(r)|^2\right)$ for hydrogen like atoms.

http://www.st-andrews.ac.uk/~qmanim/embed_item_3.php?anim_id=50

Further Reading

The explicit forms of the eigenfunctions can be found in several books, or at the url: http://panda.unm.edu/courses/finley/P262/Hydrogen/WaveFcns.html.

Further Reading



Here you find a presentation on the different possibilities of visualizing the Hydrogen atom.
http://www.hydrogenlab.de/elektronium/HTML/einleitung_hauptseite_uk.html

Further Reading

isit the Grand Orbital Table: http://www.orbitals.com/orb/orbtable.htm, where all atomic orbitals till $n = 10$ are presented.

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5: Spin and the fine structure

Objectives

In this chapter we recall the experimental evidences of the existence of spin in atomic physics. Spin is a genuinely quantum-mechanical concept, despite the term spin being reminiscent of classical spinning.

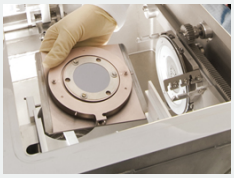
The fine structure of the spectrum was observed already in the beginning of the 20th century, but to explain it's origin theoretically, a relativistic treatment of the electron was necessary.

Prerequisites

Magnetic moment and its connection with angular momentum. The force and energy of a current loop or a magnetic moment in an external magnetic field. Chapter 3.

The Stern-Gerlach Experiment and the spin

Animation



This webpage offers a two word explanation of spin. Check out the spin tab with an animated video showing basic concepts of spin. You can also find some additional information on application of spin in technology.

http://www.toutestquantique.fr

The experiment of Stern and Gerlach, performed in 1921, was intended to look at the magnetic moment of atoms. As it is known, a magnetic momentum arises from current loops, or from charges circulating in a closed orbits, and it is still considered to be true, that a magnetic moment of a particle or a system is always proportional to its angular momentum. The hypothesis that macroscopic magnetism is also a consequence of microscopic circular atomic currents originates from Ampère.

Therefore the experiment was intended to investigate also the angular momentum of the atoms. Stern and Gerlach used silver atoms, that were evaporated from a furnace then after collimating and blending slits they obtained an atomic beam, which passed through an **inhomogeneous magnetic field**. The field of the specially shaped magnets was such that it pointed mainly to one direction, let this be the z direction. Stern and Gerlach experienced that the field caused a splitting of the atomic beam traveling originally say in the yy direction, into two beams, deviating in direction of $\mathbf{z}$ and $-\mathbf{z}$. The silver atoms are electrically neutral, therefore the bending of the atoms could not be attributed to the magnetic Lorentz force, and actually there is no such effect if the magnetic field is homogeneous. The reason of the deviation was that the atoms possessed a magnetic dipole moment, so they behaved like a magnetic needle, or a small coil and therefore the magnetic field acted on them by the force $\mathbf{F} = -\operatorname{grad}(\mathbf{mB})$, which had predominantly a z component $F_z = -\mathfrak{m}_z \frac{\partial B_z}{\partial z}$, as it was known from electromagnetism. We see that $\frac{\partial B_z}{\partial z} \neq 0$ i.e. inhomogeneity is necessary for the force to appear. This force is the reason why the silver atoms deviate from their original direction, and the amount of deviation must be proportional to the z component of the force.

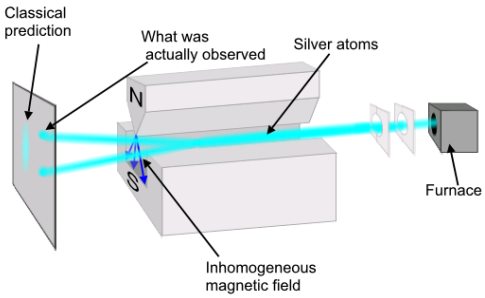
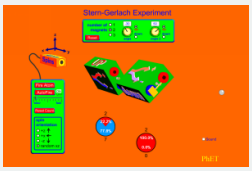


Figure 5.1: Experimental setup of the Stern-Gerlach experiment.
http://en.Wikipedia.org/wiki/File:Stern-Gerlach_experiment.PNG

Animation

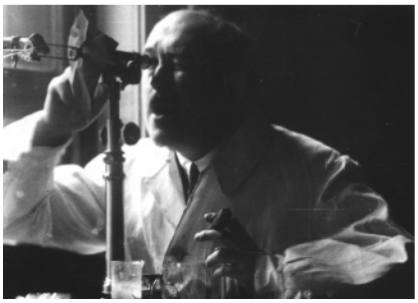


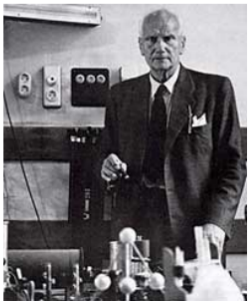
The classic Stern-Gerlach Experiment shows that atoms have a property called spin. Spin is a kind of intrinsic angular momentum, which has no classical counterpart. When the z-component of the spin is measured, one always gets one of two values: spin up or spin down.

http://phet.colorado.edu/en/simulation/stern-gerlach

We may think that the different atoms arriving into the interaction region have all possible directions of their magnetic moment, and therefore the atoms deviate in several directions depending on their $\mathfrak{m}_z$, and one obtains a continuous distribution of deviation direction. As this was not the case, and only two definitely distinct directions were observed, this proved that there must have been a kind of quantization of the direction of the magnetic momentum of the atom, and as it was supposed also in the angular momentum of the atom, which was the reason of the magnetism in particles consisting of charged constituents. The quantization of angular momentum was already known to a certain extent, but only an odd number of possibilities was predicted. According to A. Sommerfeld who already extended the old quantum model of Bohr at that time, the quantum number ℓ existed and in case of $\ell = 1$, the three possibilities of the magnetic quantum number: $m = 0, \pm 1$ was expected, instead of the observed two. What was even worse, it was known already from the spectroscopy of Ag, that its ground state is an ss state with $\ell = 0$, so the electron has no orbital angular momentum, and therefore one does not expect magnetic momentum either.

Otto Stern and Walter Gerlach





Gerlach's notice to Bohr
(1922)

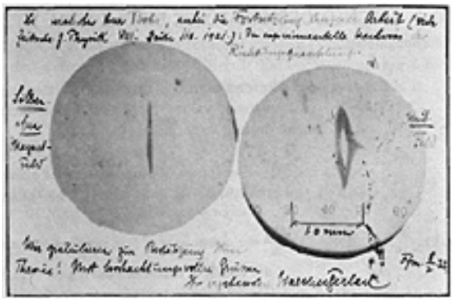


Figure 5.2:

As it turned out a few years later, the splitting was due to a new degree of freedom of atomic particles, namely the spin, which is the intrinsic angular momentum of particles, not connected with their motion in space, rather it is a kind of rotation of the particle itself, like the spinning of a ball. Although there are strong arguments that this simple picture cannot be valid, one can still visualize the spin of a particle in that way. The discovery did come from spectroscopy, S. Goudsmit and G. Uhlenbeck, the young students of P. Ehrenfest in Leiden recognized in 1926 that the fine spectrum of the H atom can be explained if one assumes that the electron possesses this intrinsic angular momentum, and

$$\mathfrak{m} = \gamma \mathbf{S} \quad (5.1)$$

where $\mathbf{S}$ is the mechanical angular momentum, which – if measured in a certain, say the z direction – can take only the two possible values $\hbar/2$ and $-\hbar/2$. This explained the result of the Stern Gerlach experiment, where only the valence electron has angular momentum, and it is a spin momentum, the angular momenta of all the other electrons add up to zero.

In view of angular momentum theory in quantum mechanics this means that the operator S_z has only two eigenstates and eigenvalues, with $m_s = \frac{1}{2}$, and $m_s = -\frac{1}{2}$, corresponding to the two discrete eigenvalues:

$$S_z\chi^+ = \tfrac{\hbar}{2}\chi^+, \quad S_z\chi^- = -\tfrac{\hbar}{2}\chi^- \quad (5.2)$$

The quantum number characterizing the total angular momentum (corresponding to ℓ) is denoted here by s, and from the analogy with the theory of angular momentum one obtains that $s = \frac{1}{2}$, as $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$, and for the eigenvalue of $\mathbf{S}^2$ we have $s(s+1)$:

$$\mathbf{S}^2\chi^\pm = \hbar^2 s(s+1)\chi^\pm = \hbar^2 \tfrac{3}{4}\chi^\pm \quad (5.3)$$

Einstein de Haas experiment

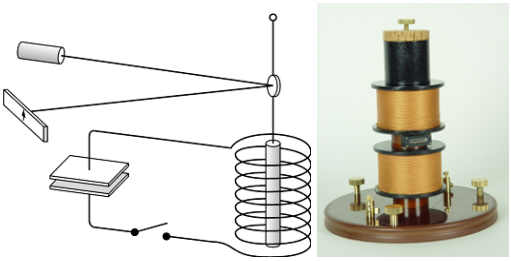


Figure 5.3: Schematic and the real setup of the Einstein-de-Haas experiment.
http://www.techniklexikon.net/d/einstein-de-haas-versuch/einstein-de-haas-versuch.htm
http://www.histodid.uni-oldenburg.de/forschung/aktuelles.htm

This was the only experiment performed by A. Einstein, and he did it in collaboration with W. J. de Haas in 1914. In the apparatus, a cylindrical iron rod was suspended on a torsion thread. Magnetization of the rod was achieved by a coil surrounding the rod with current in. Letting the current through the coil caused the cylinder to rotate by some small angle. The rotation was measured by light reflection from a mirror fixed to the sample. The effect can be explained theoretically by the fact that the magnetic moments of the atoms of the iron, being oriented in the direction of the external magnetic field, cause a change in the atomic mechanical moments – the magnetic moment M of an atom is proportional to the resultant angular momentum J, that is, $M = \gamma J$, where γ is the gyromagnetic ratio. On the basis of the law of the conservation of angular momentum, the total angular momentum of a body must remain unchanged, and upon magnetization the body therefore acquires an angular impulse (very small in magnitude) that is inverse with respect to the axis of magnetization.

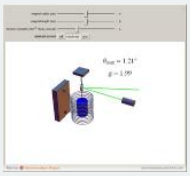
As we know now that the orbital angular momentum of the electrons in iron is zero, the reason is spin. As it is known from classical electrodynamics, in the case of a circular currents the coefficient between the magnetic and angular momentum is

$$\mathfrak{m} = \frac{q}{2m}\mathbf{L} \quad (5.4)$$

Interestingly in the case of spin angular momentum the coefficient giving the magnetic moment is twice

$$\mathfrak{m} = \frac{q}{m}\mathbf{S} \quad (5.5)$$

Animation



Einstein had long contemplated Ampère's conjecture in 1820 that magnetism is caused by circulation of electric charge. This Demonstration describes a technologically updated version of the original Einstein–de Haas experiment. The current is large enough to create a magnetic field strong enough to saturate the cylinder's magnetization in either direction. If Ampère was right, this should create an angular displacement of the magnet.

http://demonstrations.wolfram.com/EinsteinDeHaasEffect/

Spin orbit coupling and fine structure

The derivation of the energy levels for the Coulomb potential was based on the Schrödinger equation, which did not contain spin. In reality, there exist small corrections to the level structure, due to the so called spin-orbit coupling. This leads to a fine structure of the spectrum, which could be observed already in the beginning of the 20th century before the advent of modern quantum mechanics. The exact formulation of how the spin and angular momenta are coupled to each other is a difficult mathematical problem, and it necessitates a relativistic treatment of the electron. Therefore we explain here this effect by hand-waving arguments.

In the coordinate system of the electron circulating around the nucleus the proton is moving around the electron therefore in addition to the electric field there must be also a magnetic field. According to the Biot-Savart law, or more generally from Ampère's law $(\mathrm{rot}\,\mathbf{B} = \mu_0\mathbf{J})$ the field emerging from the motion of the proton is

$$\mathbf{B} = \frac{\mu_0}{4\pi}\frac{Zq_0}{m_0}\frac{\mathbf{L}}{r^3} \quad (5.6)$$

This magnetic field also interacts with the intrinsic magnetic moment of the electron, stemming from its spin, and causes an additional energy shift $\Delta E = -\mathfrak{m}\mathbf{B} = \frac{\mu_0}{4\pi}\frac{Zq_0^2}{m_0}\frac{\mathbf{s}\cdot\mathbf{L}}{r^3}$. Going back to the laboratory frame, the rest frame of the proton, an additional factor of $1/2$ arises this is due to an effect called Thomas precession, and it's reason is the **circular** motion of the two frames with respect to each other. The result of spin-orbit interaction is an energy shift

$$\Delta E = -\mathfrak{m}\mathbf{B} = \frac{\mu_0}{4\pi}\frac{Zq_0^2}{2m_0}\frac{\mathbf{S}\cdot\mathbf{L}}{r^3} = \frac{Ze_0^2}{2m_0c^2}\frac{\mathbf{S}\cdot\mathbf{L}}{r^3} \quad (5.7)$$

where the last equality comes from the definition $e_0^2 = q_0^2/4\pi\epsilon_0$ and $\epsilon_0\mu_0 = c^{-2}$. We note again that this result can be deduced strictly from the relativistic quantum mechanical equation of the electron, the famous Dirac equation, which we will not considered here. The operator product $\mathbf{S}\cdot\mathbf{L}$ can be calculated as follows. First, one defines the total angular momentum:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (5.8)$$

which is a conserved quantity in a central field, in contrast to $\mathbf{L}$ or $\mathbf{S}$ separately. We square this sum and obtain

$$\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\mathbf{S} \quad (5.9)$$

as $\mathbf{L}$ and $\mathbf{S}$ are commuting operators. Then

$$\mathbf{L}\mathbf{S} = \tfrac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right) \quad (5.10)$$

As the eigenvectors of the Hamilton operator are eigenvectors of all the three operators $\mathbf{J}^2$, $\mathbf{L}^2$, and $\mathbf{S}^2$, with the respective eigenvalues $\hbar^2 j(j+1), \hbar^2 l(l+1), \hbar^2 s(s+1)$, the energy correction due to the spin orbit interaction is

$$\Delta E = \frac{\beta}{2}\left(j(j+1) - l(l+1) - s(s+1)\right) \quad (5.11)$$

where the spin-orbit coupling strength is given by

$$\beta = \frac{Ze_0^2}{2m_0c^2}\frac{\hbar^2}{r^3} = \frac{\mu_0}{4\pi}\frac{Zq_0^2}{2m_0}\frac{\hbar^2}{r^3} \quad (5.12)$$

If we want to find explicitly the effect of this term we have to calculate its expectation value in a state ψ_{nlm}. In order to do so, we have to calculate the following integral with the eigenfunctions $\psi_{nlm}(\mathbf{r}) = \frac{u_{nl}(r)}{r}Y_\ell^m(\theta,\phi)$

$$\int \psi_{nlm}^*(\mathbf{r})\frac{1}{r^3}\psi_{nlm}(\mathbf{r})d^3\mathbf{r} = \int_0^\infty \frac{u_{nl}^2(r)}{r^2}\frac{1}{r^3}r^2dr = \int_0^\infty \frac{u_{nl}^2(r)}{r^3}dr \quad (5.13)$$

with the radial functions $u_{nl}(r)$ determined in the previous section. The integration with respect to the angular variables gives unity, in view of the normalization of the spherical harmonics. The integration can be done using the properties of the Laguerre polynomials, or by some other tricks and yields the result $\frac{2Z^3}{a_0^3 n^3 l(l+1)(2l+1)}$ which gives

$$\beta(n,l) = \frac{Z^4e_0^2}{2m_0c^2}\hbar^2\frac{1}{a_0^3n^3l(l+1/2)(l+1)} \quad (5.14)$$

Another contribution to the fine structure of the H atom comes from the relativistic correction to the kinetic energy. In relativity the kinetic energy of a particle is

$$E_{kin} = \sqrt{m_0^2c^4 + c^2p^2} - m_0c^2 = m_0c^2\sqrt{1+\frac{p^2}{m_0^2c^2}} - m_0c^2 \approx \frac{p^2}{2m_0} - \frac{p^4}{8c^2m_0^3} \quad (5.15)$$

where the approximation is valid up to second order in p/m_0c. The first term is the ordinary nonrelativistic kinetic energy, while the second one is the correction. Now – as it is customary in quantum mechanics we – consider this term as an operator, and calculate its expectation value in the $\psi_{nlm}(\mathbf{r})$ states. To this end we apply the operator $P^4 = \hbar^4\Delta^2 = \hbar^4\nabla^4$ and calculate

$$\Delta E_r = -\frac{\hbar^4}{8c^2m_0^3}\int\psi_{nlm}^*(\mathbf{r})\nabla^4\psi_{nlm}(\mathbf{r})d^3\mathbf{r} = -E_{nr}\frac{Z^2\alpha^2}{n}\left(\frac{3}{4n} - \frac{1}{l+1/2}\right) \quad (5.16)$$

Here α is the **fine structure constant** introduced by A. Sommerfeld

$$\alpha = \frac{q_0^2}{4\pi\epsilon_0}\frac{1}{\hbar c} = \frac{e_0^2}{\hbar c} = 7.297\times10^{-3} = \frac{1}{137} \quad (5.17)$$

which is a dimensionless quantity, playing an important role in atomic physics and in quantum electrodynamics.

In order to obtain the total correction one has to add the two terms yielding

$$E_{nj} = E_n \left[1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \quad (5.18)$$

Importantly the same result is obtained from Dirac's exact relativistic theory in second order in p/m_0c.

As a result the ground state energy of the H atom, where $n = 1$, $j = 1/2$ is lowered by , and a similar shift is valid for all the ss states. Additionally there is a splitting with respect to the nonrelativistic result, causing the fine structure in the observed lines. Namely for a given ll one has two possible *j*-s, $j = l + 1/2$ and $j = l - 1/2$, except for $l = 0$. The splitting between the $2p_{3/2}$ and the $2p_{1/2}$ levels is $\Delta E = 4.6 \times 10^{-6}\text{eV}$. Corresponding to a difference in wave number $\Delta\bar{\nu} = 0.37\ \text{cm}^{-1}$.

Animation

We can investigate the relativistic energy levels for Hydrogen atom with this interactive animation. The fine-structure constant can be conceptually changed from 0 to its actual value, or equivalently the speed of light *c* from ∞ to 1 (meaning $3 \cdot 10^8\ \text{m/s}$), to show the transition from nonrelativistic to relativistic energies for quantum numbers $n = 1, 2 \text{ and } 3$.

http://demonstrations.wolfram.com/RelativisticEnergyLevelsForHydrogenAtom/

Hyperfine structure

A more refined spectroscopic investigation revealed that even the fine structure components of the H atom are split into two subcomponents and a similar doublet structure was observed in several other atoms. It turned out, that this splitting was due the interaction of the magnetic moment of the nucleus, and the electrons.

In the case of the H atom the simple picture is the following. The proton has a magnetic moment just like the electron. If the two magnetic momenta are antiparallel, then a magnetic attraction appears so the energy will be lower than for parallel moments. So these two possibilities lead to an extra splitting of the $1s$ ground state, and a smaller splitting of other states, as well.

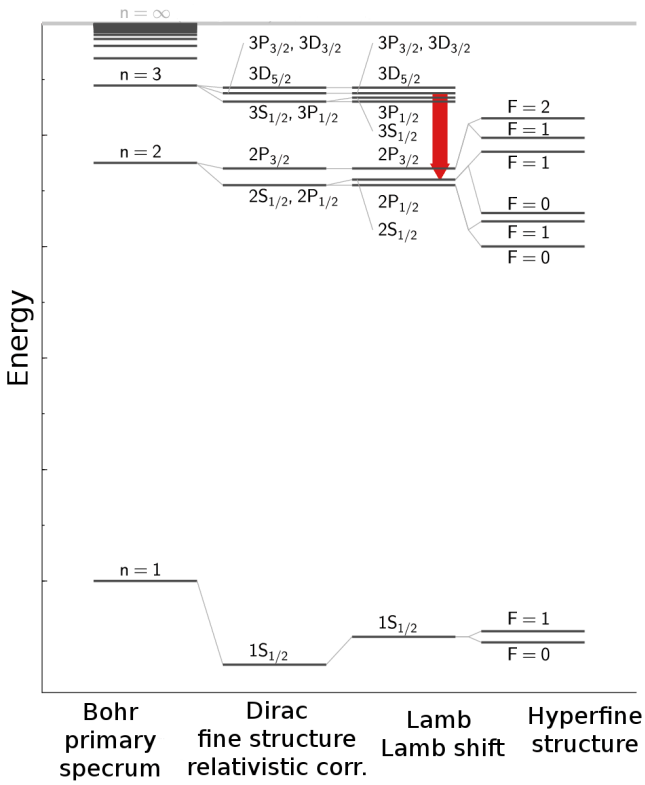


Figure 5.4: The hierarchy of energy shifts of the spectra of hydrogen-like atoms as a result of relativistic corrections. The first column shows the primary spectrum. The second column shows the fine structure from relativistic corrections. The third column includes corrections due quantum electrodynamics and the fourth column includes interaction terms with nuclear spin The H-α line, particularly important in the astronomy, is shown in red

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6: Many-body problems, systems of identical particles

Objectives

So far we have considered single particle problems, a particle moving in a given potential. In the model of the H atom considered previously the potential was given apriori by the Coulomb field of the proton. In a physical system, however, one has usually several particles that interact with each other. In reality already the H atom consists of two particles: a proton which is the nucleus and the electron.

Prerequisites

Chapters 2, 4 and 5. The two-body problem in classical mechanics.

Entanglement of two particles

In order to see the peculiarities of the situation, we shall consider, as an example, the case of the H atom as **a two-body problem**. The wave function of such a system should depend on the coordinates of the electron $\mathbf{r}_e$ as well as on the coordinates of the proton $\mathbf{R}_n$, where *n* refers to the nucleus. The Hamiltonian of this two particle system is

$$H_{ne} = \frac{\mathbf{P}_n^2}{2M_n} + \frac{\mathbf{P}_e^2}{2m_e} - \frac{e_0^2}{|\mathbf{R}_n - \mathbf{r}_e|} \quad (6.1)$$

and the wave function $\Psi(\mathbf{r}_e, \mathbf{R}_n, t)$ must obey:

$$i\hbar \frac{\partial \Psi(\mathbf{r}_e, \mathbf{R}_n, t)}{\partial t} = H_{ne}\Psi(\mathbf{r}_e, \mathbf{R}_n, t) = \left(\frac{\mathbf{P}_n^2}{2M_n} + \frac{\mathbf{P}_e^2}{2m_e} - \frac{e_0^2}{|\mathbf{R}_n - \mathbf{r}_e|}\right)\Psi(\mathbf{r}_e, \mathbf{R}_n, t) \quad (6.2)$$

Among all the solutions, those corresponding to stationary states of the system are specific, and have the form:

$$\Psi(\mathbf{r}_e, \mathbf{R}_n, t) = \psi_\varepsilon(\mathbf{r}_e, \mathbf{R}_n)\, e^{-i\varepsilon t/\hbar} \quad (6.3)$$

where ε is one of the eigenvalues of H and the corresponding eigenfunction is $\psi_\varepsilon(\mathbf{r}, \mathbf{R})$

$$H\psi_\varepsilon(\mathbf{r}_e, \mathbf{R}_n) = \varepsilon\psi_\varepsilon(\mathbf{r}_e, \mathbf{R}_n) \quad (6.4)$$

The eigenfunctions are then functions of the variables $\mathbf{r}_e, \mathbf{R}_n$: The form of the Hamiltonian depending only on their difference allows us a separation if one introduces new coordinates and momenta in the form:

$$\begin{aligned} \mathbf{R}_0 &= \frac{M_n\mathbf{R}_n + m_e\mathbf{r}_e}{M_n + m_e}, & \mathbf{P}_0 &= \mathbf{P}_n + \mathbf{P}_e \\ \mathbf{r} &= \mathbf{r}_e - \mathbf{R}_n, & \mathbf{P} &= \frac{M_n\mathbf{P}_e - m_e\mathbf{P}_n}{m_e + M_n} \end{aligned} \quad (6.5)$$

Here $\mathbf{R}_0$ is the centre of mass coordinate of the two body problem, and $\mathbf{P}_0$ is the total momentum of the electron and the nucleus. On the other hand $\mathbf{r}$ is the relative coordinate and $\mathbf{P}$ is the relative momentum of the two particles.

Problem 6.1

Show that in these new variables the Hamiltonian takes the form:

$$H_{ne} = \frac{\mathbf{P}_0^2}{2M} + \frac{\mathbf{P}^2}{2m} - \frac{e_0^2}{|\mathbf{r}|} \quad (6.6)$$

with $M = M_n + m_e$ and $m = \frac{M_n m_e}{M_n + m_e}$.

Problem 6.2

Using the canonical commutation relations show the following results:

$$\begin{aligned} [R_{0i}, P_{0j}] &= i\hbar\delta_{ij}, \quad [r_i, P_j] = i\hbar\delta_{ij} \\ [R_{0i}, P_j] &= 0, \quad [r_i, P_{0j}] = 0 \end{aligned} \quad (6.7)$$

and all the other commutators vanish.

We see that the Hamiltonian separates into two **independent** parts: $H_{\text{ne}} = H_0 + H$, where $H_0 = \frac{\mathbf{P}_0^2}{2M}$ describes a free particle, which is the system as a whole, whereas $H = \frac{\mathbf{P}^2}{2m} - \frac{e_0^2}{|\mathbf{r}|}$ corresponds to the relative motion of the constituents. In such cases where the two Hamiltonians H_0 and H are independent the solution of the eigenvalue problem of their sum is simple. One solves separately the two eigenvalue equations:

$$\begin{array}{c} H_0\varphi\left(\mathbf{R}_0\right) = \varepsilon_0\varphi\left(\mathbf{R}_0\right) \\ H\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \end{array} \quad (6.8)$$

and it is simply to see that the stationary solutions of the composite problem are

$$\varphi\left(\mathbf{R}_0\right)\psi(\mathbf{r})e^{-i(\varepsilon_0+\varepsilon)t/\hbar} \quad (6.9)$$

If we wish to get back, however, separately the wave functions of the nucleus and the electron, we see that this is impossible.

If we substitute back into (6.9) their original coordinates, we get $\varphi\left(\frac{M_n\mathbf{R}_n+m_e\mathbf{r}_e}{M_n+m_e}\right)\psi\left(\mathbf{r}_e-\mathbf{R}_n\right)$ and we see that the two particles lose their individual wave functions, the energy eigenfunctions will not be products of functions of the electron coordinates and of the nuclear coordinate. Such a state is called an **entangled state**, and in the case of interacting particles this is always the case, only the system as a whole has a definite state, the constituents do not.

From the point of view of the explicit solution by the separation method the above example of the H atom can be generalized to any two body problem, irrespective of the form of the potential. We used the fact that the interaction depended only on the difference of the coordinates, but it could have been any other function of $\mathbf{r} = \mathbf{r}_e - \mathbf{R}_n$, the separation trick we made would have worked. This is similar to the case of any two body problem in **classical mechanics**, which can always be reduced to a centre of mass and a relative motion. However when the system consists of more than two particles, the separation is impossible in general either in classical or in quantum mechanics. What remains specific in the quantum case is the entanglement which complicates the treatment further.

The main conclusion of this section is that a system of several particles is in general in an entangled state which means that its wave function $\psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N\right)$ cannot be written as a product of functions of the variables of the separate constituents.

Systems of identical particles, bosons and fermions

Indistinguishable particles

In quantum mechanics the problem of several particles is even more complicated, if these are **identical** particles. According to our present knowledge two electrons or two photons are indistinguishable, or in other words, they are identical. In the case of electrons e.g. this means that the intrinsic properties: mass, electric charge, spin angular momentum are the same for all electrons in the world. Let us note that this can be far from trivial when a new particle is discovered. When neutrinos were observed, first they were thought to be all identical. It turned out only later, that neutrinos differ from their antiparticles from the antineutrinos, and even later it became also clear that other kinds of neutrinos also existed e.g. the muonic neutrinos were recognized to be different from the electron neutrinos, they took part in different reactions, etc.

The important fact is that there exist identical particles in nature, and they are indistinguishable, and this property bears very important implications with respect to a system of such particles.

The symmetrization postulate

In quantum physics the particle can be characterized by its spatial probability amplitude and by its spin projection on a selected axis. We know that if the particle has an intrinsic angular momentum, spin *s*, which can be $0, 1/2, 1, 3/2 \ldots$,depending on the sort of the particle, then its projection on a selected axis, m_s to be abbreviated here simply by *m*. It can take the $2s+1$ different values $-s, -s+1 \ldots, s-1, s$. From now on the coordinate and the spin projection variable associated jointly with the *k*-th particle will be denoted by $\xi_k = (\mathbf{r}_k, m_k)$.

One might assume that the wave function of the system of several particles, say electrons could be **any square integrable function** of the $\xi_k, k = 1, 2 \ldots N$, as it is the case for different particles like for the electron and the proton, in the H atom. But it turns out that **such an assumption** leads to consequences that **contradict experimental observations**. In reality there exist a severe restriction on the form of the possible wave functions, and this restriction depends on the spin quantum number ss of the particles in question, and we give here these rules as postulates.

First we state the postulate for particles with **integer spin** like the photon or the pions etc. and then separately for particles having **half integer spin** like the electron, proton, muon etc.

- The postulate for identical particles with integer intrinsic spin $s = 1, 2, \ldots$ states that their wave function as a whole must be symmetric with respect to the interchange of its variables, which means that any permutation of the arguments must give one and the same multiparticle function:

$$\psi\left(\xi_1, \xi_2, \ldots \xi_N\right) = \psi\left(\xi_{i_1}, \xi_{i_2}, \ldots \xi_{i_N}\right) \text{ (6.10)}$$

where $i_1, i_2, \ldots i_N$ is an arbitrary permutation of the numbers $1, 2 \ldots N$.

- The postulate for identical particles which have half integer intrinsic spin: $s = 1/2, 3/2, \ldots$ that the wave function must be antisymmetric with respect to the interchange of its variables. This means that the wave function must change its sign if any two of the arguments referring to two particles are interchanged, e.g..

$$\psi\left(\xi_1, \xi_2, \xi_3 \ldots \xi_N\right) = -\psi\left(\xi_2, \xi_1, \xi_3 \ldots \xi_N\right) \text{ (6.11)}$$

As we know, there are $N!$ different orders (permutations) of the N variables, and it can be shown by a mathematical theorem, that a given permutation can be achieved **either by an even or by an odd number of transpositions** (interchanges of two variables) from the original order. Additionally these two cases are mutually exclusive. In other words a permutation has a well defined parity, although the transpositions to reach a given permutation can be done in several different ways, and their number can be also different, but their parity is always identical. A permutation of the N objects (numbers) is called even or odd, depending on the number of transpositions to reach it from the starting order. If the order of the arguments of the function is an even permutation, then the antisymmetric wave function does not change its sign, while in the case of an odd one, there must be a sign change of the wave function.

These requirements restrict strongly the possible wave functions for identical particles. We say that the particles with **symmetric wave functions** follow the **Bose statistics**, and they are **called bosons**, while the particles with **antisymmetric** wave functions obey **Fermi statistics** and they are called **fermions**. According to what we have said above, **particles with integer spin are bosons**, while **those with half integer spin are fermions**. The difference between the symmetric and antisymmetric states has strong and macroscopically observed consequences. We come to these in the next sections.

Independent particles

Very often in atomic, molecular or solid state physics we treat the many particle system as if there were no interaction between the individual particles. This is exact, for instance, in the case of the photons representing the electromagnetic field in a cavity, because photons do not interact with each other, they are really independent. But for an atom with several electrons, these repel each other due to their electric charge, so there is an interaction between them. Then, strictly speaking, only the wave functions of the whole system of electrons exist in the field of the nucleus, it makes no sense to speak of the state of a single electron. In many cases, however, even for electrons we can **approximate** the collective system as an ensemble of independent ones, which is a good approximation if the volume density of the constituents is not too large. For instance a metal consists of a great number of electrons which can be considered at least approximately as a gas of electrons, and their interaction can be neglected. This is the Drude-Sommerfeld model, which yields already good results, if the antisymmetrization postulate for electrons is taken into account. We shall first consider the independent particle model for bosons, and then for fermions.

System of independent bosons

A simple example for a many body problem is a system of independent bosons, e.g. of Hydrogen atoms, where the total spin is integer, as both the proton and the electron has a spin $s = 1/2$, thus they can add up to either to 0, when they are antiparallel or to 1, when they are parallel. If we assume that the interaction between the atoms can be neglected, and we do not consider their internal structure, then this gas of atoms can be described by a Hamilton operator

$$H = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2M_a} = \sum_{i=1}^{N} h(i) \text{ (6.12)}$$

where M_a is the identical mass of each of the particles, the summation goes over all the number of the particles, which are seen to be independent, as the H operator is a sum of independent terms. As we see this Hamilton operator does not depend on the spin variable.

Specific and mathematically correct solutions of the eigenvalue equation are

$$H\Psi(\mathbf{r}_1,\mathbf{r}_2,\dots\mathbf{r}_N)=\left(\sum_i h(i)\right)\Psi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N)=\mathcal{E}\Psi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N)\quad(6.13)$$

and can be written as a product of so called **one particle eigenstates** $\varphi_{\alpha_i}(\mathbf{r}_i)$:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N)=\varphi_{\alpha_1}(\mathbf{r}_1)\varphi_{\alpha_2}(\mathbf{r}_2)\dots\varphi_{\alpha_N}(\mathbf{r}_N)\quad(6.14)$$

where each factor in this product obeys:

$$h(i)\varphi_{\alpha_i}(\mathbf{r}_i)=\varepsilon_{\alpha_i}\varphi_{\alpha_i}(\mathbf{r}_i)\quad(6.15)$$

and

$$\mathcal{E}=\sum_i\varepsilon_{\alpha_i}\quad(6.16)$$

Note that each one-particle Hamiltonian $h(i)$ in (6.15) has several eigenvalues and eigenstates, these are labelled by the indices α_i: ε_{α_i} and $\varphi_{\alpha_i}(\mathbf{r}_i)$, and as in our case all the particles are identical, the set of possible α_i-s are the same for all *i*-s. These functions can even be given explicitly if the boundary conditions are simple (say, if the gas is in a box), but we shall not discuss their explicit form. Although we considered a Hamiltonian that is spin independent, in principle the one-particle wave function should be completed by a spin factor (spinor) χ_s^m, and to consider the product $\varphi_{\alpha_i}(\mathbf{r}_i)\chi(i)_s^m=:\varphi(\mathbf{r}_i,m_i)=\varphi(\xi_i)$.

For the sake of simplicity in the case of bosons we shall consider only particles with $s=0$, which means that the spin does not play any role, and the single particle states are completely determined by the coordinate wave functions $\varphi_{\alpha_i}(\mathbf{r}_i)$.

The important fact is that the many-particle function $\Psi(\mathbf{r}_1\mathbf{r}_2,\dots\mathbf{r}_N)$ in (6.14) is not a symmetric function, in general, as required by the symmetrization postulate except for the specific case, where all the indices α_i are identical, which means that all the particles are in the same one-particle state. The interesting specific case, when this identical state belongs to the lowest one particle energy will be discussed in the next subsection.

In order to see the solution in general let us see first the case of two bosons. We take two one particle functions out of the solutions, say $\varphi_1(\mathbf{r}_1)$ and $\varphi_2(\mathbf{r}_2)$. Their product $\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)$ is not symmetric: if we change $\mathbf{r}_1\leftrightarrow\mathbf{r}_2$ the product will be another function of its variables. Therefore we symmetrize the product by taking the symmetric linear combination

$$\Psi_S(\mathbf{r}_1,\mathbf{r}_2)=\mathcal{N}\{\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)+\varphi_1(\mathbf{r}_2)\varphi_2(\mathbf{r}_1)\}\quad(6.17)$$

where $\mathcal{N}$ is an appropriate normalization constant, and which already obeys the symmetry requirement for bosons: the change $\mathbf{r}_1\leftrightarrow\mathbf{r}_2$, does not change anything $\Psi_S(\mathbf{r}_1,\mathbf{r}_2)=\Psi_S(\mathbf{r}_2,\mathbf{r}_1)$. This procedure is not necessary if we choose at the beginning two identical one particle functions for both particles, say φ_1. Then we would have $\Psi_S(\mathbf{r}_1,\mathbf{r}_2)=\varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$, which is obviously symmetric with respect to $\mathbf{r}_1\leftrightarrow\mathbf{r}_2$. This means that the two particles (bosons) can be simultaneously in the same quantum state. As we shall see, this will be impossible for fermions.

Problem 6.3

Let $\varphi_1(\mathbf{r}_1),\varphi_2(\mathbf{r}_2),\varphi_3(\mathbf{r}_3)$ three different one particle functions. Find their symmetrized combination. Assume now that two of them, say φ_1 and φ_2 are identical. What is the symmetrized combination? What is the result if all three functions are identical? Assume that the one particle functions are orthogonal if they are different and normalized. Take care of the normalization of the symmetric combination.

Problem 6.4

Show that if $\varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)$ is a solution of the eigenvalue problem (6.13), then so does (6.17).

The ground state of independent bosons

The quantum state of a system, which has the lowest total energy $\mathcal{E}_0$ is called the ground state. If a system has discrete energy levels, and the lowest one is far below the next first excited energy state $\mathcal{E}_1$, then at low temperatures $(\mathcal{E}_1-\mathcal{E}_0\gg k_BT)$ the system will be found in its ground state with a probability close to 1. The lowest energy of a system of independent bosons will be a state where all the particles are in their identical lowest energy one-particle state φ_0 with energy ε_0. Then the *N*-fold product of these states

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N)=\varphi_0(\mathbf{r}_1)\varphi_0(\mathbf{r}_2)\dots\varphi_0(\mathbf{r}_N)\quad(6.18)$$

is automatically symmetric with respect to all changes in the arguments, and the total energy is

$$\mathcal{E}_0 = N\varepsilon_0 \quad (6.19)$$

This state of the gas of bosons is called a Bose-Einstein condensate (BEC).

There are other, less stringent, statistical definitions for this very exceptional quantum state of a bosonic system, where not all, but only the vast majority of the atoms are found in their lowest one-particle state. When the states of the system above the ground state form a continuous set, then it is not simple to achieve the condensation, i.e. to push the majority of the particles into the ground state, because the temperature must be very low. We come back to a detailed discussion of producing a Bose-Einstein condensates in chapter 8.

System of independent fermions

An important example of an independent many fermion system is the gas of the electrons in a metal, as they can be considered as noninteracting in the first approximation. Their Hamiltonian is then again (6.12)

$$H = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2m_e} = \sum_{i=1}^{N} h(i) \quad (6.20)$$

where $\mathbf{P}_i$ is the momentum operator of the *i*-th electron and m_e is now the mass of the electron. The considerations in the beginning of the previous section do not change, so all the formulae (6.13), (6.14), (6.15) and (6.16) remain valid in this case, as well. The product (6.14) is however only a mathematically allowed solution. This was the case for a bosonic system where the product had to be symmetrized. In the case of fermions the postulate requires the antisymmetrization of the product. The Hamiltonian is not spin dependent in this case either, but the spin of the particles still plays an important role in the construction of the total wave function. Now we have to complete the single particle functions with a spin part, as well. In the most frequent case, e.g. for electrons, we have $s = 1/2$, and then we have two choices with $m_i = +1/2 : \chi^+(i)$ and $m_i = -1/2 : \chi^-(i)$ for short, and the total one-electron function is $\varphi(\mathbf{r}_i)\chi^{\pm}(i) =: \varphi(\xi_i)$, where ξ_i stands for both $\mathbf{r}_i$ and m_i of the spin.

We begin the antisymmetrization with two particles. Assume that we know that one of the particles is in the state given by $\varphi(\xi_i)$ while the other is in $\psi(\xi_i)$. We assume here that these one particle functions are normalized. The physical state for the two independent fermions is given then by:

$$\Psi_A(\xi_1, \xi_2) = \mathcal{N}\{\varphi(\xi_1)\psi(\xi_2) - \varphi(\xi_2)\psi(\xi_1)\} \quad (6.21)$$

where $\mathcal{N}$ is a normalization factor. If φ and ψ are orthogonal, then $\mathcal{N} = 1/\sqrt{2}$. . We see that this function is antisymmetric, as if we change the indices $1 \leftrightarrow 2$, then $\Psi_A(\xi_1, \xi_2)$ changes sign, i.e. $\Psi_A(\xi_1, \xi_2) = -\Psi_A(\xi_2, \xi_1)$ We also see, that this wave function automatically satisfies the Pauli principle in its elementary form, as if φ and ψ were identical then $\Psi_A(\xi_1, \xi_2)$ would become zero, thus a state, where both fermions (electrons) are in the same one-particle quantum state does not exist.

Problem 6.5

Show that (6.21) is a solution of (6.13) with $\mathcal{E} = \varepsilon_\varphi + \varepsilon_\psi$.

Note that the above two particle state (6.21) can be written as a determinant:

$$\Psi_2(\xi_1, \xi_2) = \mathcal{N}\begin{vmatrix} \varphi(\xi_1) & \varphi(\xi_2) \\ \psi(\xi_1) & \psi(\xi_2) \end{vmatrix} \quad (6.22)$$

For N independent particles the antisymmetrization is a generalization of this latter form. If the one particle states are $\varphi_1(\xi_1), \varphi_2(\xi_2) \ldots \varphi_N(\xi_N)$, then for fermions we construct the determinant.

$$\Psi(\xi_1, \xi_2, \ldots \xi_N) = \mathcal{N}\begin{vmatrix} \varphi_1(\xi_1) & \varphi_1(\xi_2) & \ldots & \varphi_1(\xi_N) \\ \varphi_2(\xi_1) & \varphi_2(\xi_2) & \ldots & \varphi_2(\xi_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\xi_1) & \varphi_N(\xi_2) & \ldots & \varphi_N(\xi_N) \end{vmatrix} \quad (6.23)$$

which is called a **Slater-determinant**. If two or more one-particle states are identical, the determinant vanishes, and it is antisymmetric with respect of any change of two of the particles.

The ground state of independent fermions

The lowest energy many-particle state should be also a Slater determinant (6.23) where the φ_{α_j} functions are all different, otherwise the determinant would vanish, but the corresponding one-particle energies ε_j are not necessarily different as the one-electron energies can be degenerate, and therefore particles can be "put" into different orthogonal states that have identical energies. Let us label the one-particle eigenvalues with their increasing values as

$$\varepsilon_0 < \varepsilon_1 < \varepsilon_2 \ldots \quad (6.24)$$

and let the corresponding degrees of degeneracies $g_0, g_1, g_2, \ldots$, meaning that there are g_i different orthogonal solutions φ_i of $h\varphi_i = \varepsilon_i \varphi_i$ belonging to the same ε_i. The lowest possible energy of the *N* particle system is realized if one fills the states with the lowest possible one-electron energies, but this means no more states than the degeneracy of the given energy. The total energy in this case is

$$\mathcal{E}_0 = g_0\varepsilon_0 + g_1\varepsilon_1 + \ldots + g_{n-1}\varepsilon_{n-1} + \left(N - \sum_{k=0}^{n-1} g_k\right)\varepsilon_n \quad (6.25)$$

where *n* is the smallest integer for which $g_0 + g_1 + \ldots + g_n \geq N$.

If the *N* particle system is in its ground state with energy $\mathcal{E}$, then the highest one-electron energy level which is still populated is called the Fermi level or Fermi energy. It plays an important role in the electronic structure of macroscopic solid bodies, in metals or semiconductors. As in these materials at room temperatures, only those electrons are excited thermally which possess an energy of ε_F or less by only about k_BT. This number is many orders of magnitude less than the number of all the electrons *N*, which has important consequences from the point of view of thermal properties of solids. A more detailed discussion of these questions is the subject of statistical physics and solid state physics.

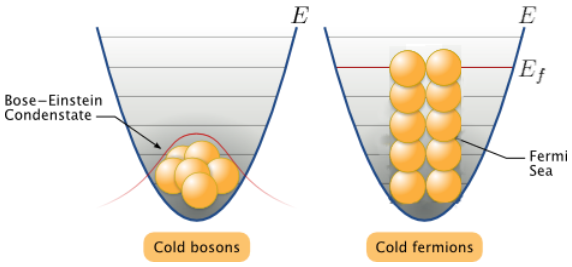
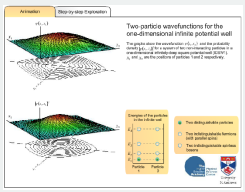


Figure 6.1: As the temperature drops near absolute zero, the gas of bosons collapses, forming a Bose-Einstein Condensate. Fermions cannot reach this state, since they can't occupy the same quantum state. The total energy of the Fermi gas is then larger than the sum of the single-particle ground state. The energy of the highest occupied quantum state is called the Fermi energy.
http://quantum-bits.org/?p=233

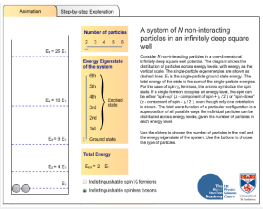
Animation



This flash animation shows you some examples of the above symmetrization postulates in case of two-particle wavefunctions for the one dimensional infinite potential well. Three different cases are demonstrated, namely two distinguishable particles, two fermions with parallel spin and two bosons with zero spin.

http://www.st-andrews.ac.uk/~qmanim/embed_item_3.php?anim_id=3

Animation



This flash animation guides you through the case of *N* non-interacting particles in an infinitely deep square well.

http://www.st-andrews.ac.uk/~qmanim/embed_item_3.php?anim_id=48

The one-electron approximation in atoms

The discussion given in the previous section can be extended to the approximate treatment of the electronic structure of atoms consisting of a nucleus with *Z* protons and a number *N* of identical electrons. The stationary states are the eigenfunctions of the following Hamiltonian:

$$H = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2m_e} - \sum_{i=1}^{N} \frac{Zq_0^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{R}_i|} + \frac{q_0^2}{4\pi\epsilon_0} \sum_{j<i} \sum_{i=1}^{N} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (6.26)$$

where we consider the nucleus fixed. In spite of the interaction described here by the third term, a surprisingly good approximation can be obtained by an iterated independent particle model, which we shall explain here. Let us note that the form of this Hamiltonian is a simplified one, there are in general spin dependent terms not contained in (6.26), but they can be neglected in the first approximation. Still, as we shall see, the spin of the particles shall influence the states indirectly through the antisymmetrization postulate given in the previous section.

It is impossible to determine the exact form of the spatial wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ by analytic or even by numerical methods, as it will be a function of $3N$ variables in the spin independent case. Therefore we shall use the **one-electron approximation**, where we assume that if we consider a single electron separately from all the others, and the **electron-electron interaction term** (the last term in (6.26)) **can be approximated by a potential energy of that single electron in the field of all the others**. This potential energy function, which is to be written as $V(\mathbf{R}_i)$ for the *i*-th electron, should depend only on the coordinate of that single electron. Mathematically this means that we make the following replacement

$$\sum_{i,j,i<j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \longrightarrow \sum_i V(\mathbf{R}_i) \quad (6.27)$$

So far we do not know the explicit form of $V(\mathbf{R}_i)$, but the procedure we explain below will also yield us the expression of this potential energy. It may seem that we distinguish between the electrons by taking out one, but as we will see later, this will not be the case. We have then the following approximate Hamiltonian:

$$H^i = \sum_i h(i) \quad (6.28)$$

where now

$$h(i) = \frac{\mathbf{P}_i^2}{2m} - \frac{Ze_0^2}{R_i} + V(\mathbf{R}_i) \quad (6.29)$$

is an **effective one-electron operator** that depends only on the coordinates of a single electron. Assume that we can find the solutions of the one-electron problem:

$$h(i)\varphi_{\alpha_i}(\mathbf{r}_i) = \varepsilon_{\alpha_i}\varphi_{\alpha_i}(\mathbf{r}_i) \quad (6.30)$$

then the solution of

$$H^i\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_i h(i)\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \mathcal{E}\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \quad (6.31)$$

can be written as a product of so called **one particle eigenstates** $\varphi_{\alpha_i}(\mathbf{r}_i)$:

$$\Psi_H(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \prod_{\alpha_i} \varphi_{\alpha_i}(\mathbf{r}_k) = \varphi_{\alpha_1}(\mathbf{r}_1)\varphi_{\alpha_2}(\mathbf{r}_2)\ldots\varphi_{\alpha_N}(\mathbf{r}_N) \quad (6.32)$$

$$\mathcal{E} = \sum_i \varepsilon_{\alpha_i} \quad (6.33)$$

Ψ_H is a so called Hartree function, after D. Hartree, who first applied this approximation for multielectron atoms. The problem with Ψ_H is that it is not antisymmetric as prescribed by the antisymmetrization postulate, but we come soon to this point.

Problem 6.6

Show the validity of (6.31).

The method of Hartree intended to determine the ground state energy of the composite system. To this end he had chosen an initial set of *N* **different** wave functions, usually the well known eigenstates of lowest energy in a H-like atom with nuclear charge *Z*. The potential energy of the *i*-th single electron in the field of all others can be expressed by the spatial charge density of the other electrons:

$$\sum_{jeqi} \varrho\left(\mathbf{r}_j\right) = \sum_{jeqi}^{N} e_0^2 \left|\varphi_j\left(\mathbf{r}_j\right)\right|^2 \quad (6.34)$$

according to

$$V\left(\mathbf{r}_i\right) = \sum_{jeqi}^{N} \int \frac{e_0^2 \left|\varphi_j(\mathbf{r}_j)\right|^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} d^3\mathbf{r}_j \quad (6.35)$$

This is the Coulomb potential of the *i*-th electron created by the charge density of the other ones, and this is the effective one-electron potential. Now we can add this potential to the one-electron Hamiltonian, and we can solve the eigenvalue equation:

$$\left(-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze_0^2}{R_i} + V\left(\mathbf{r}_i\right)\right)\varphi_i\left(\mathbf{r}_i\right) = \varepsilon_i \varphi_i\left(\mathbf{r}_i\right) \quad (6.36)$$

which will yield us new one-electron eigenfunctions $\varphi_i(\mathbf{r}_i)$ and energies ε_i. From these functions we select those belonging to the lowest energy, and construct again a potential of the form (6.35), and then solve (6.36). In the *k*-th step of this iteration we solve thus

$$\left(-\frac{\hbar^2}{2m}\Delta_i - \frac{Ze_0^2}{R_i} + \sum_{jeqi}^{N} \int \frac{e_0^2 \left|\varphi_j^{(k-1)}(\mathbf{r}_j)\right|^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} d^3\mathbf{r}_j\right) \varphi_i^{(k)}\left(\mathbf{r}_i\right) = \varepsilon_i^{(k)} \varphi_i^{(k)}\left(\mathbf{r}_i\right). \quad (6.37)$$

The procedure is to be repeated until the resulting potential differs from the one we started from by a given precision. The method is called therefore a **self consistent field (SCF) method**. In this way we can determine the charge density and the total energy of the ground state.

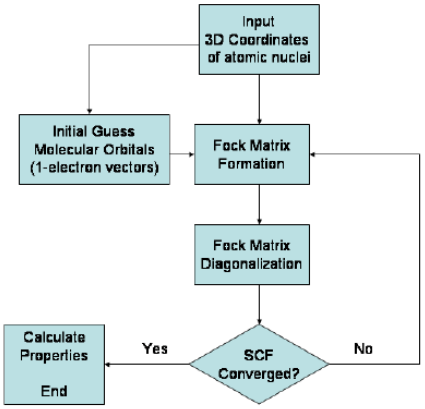


Figure 6.2: Simplified algorithmic flowchart illustrating the Hartree–Fock Method.
http://en.Wikipedia.org/wiki/Hartree-Fock_method

A serious problem with the SCF method of Hartree was, however, that in (6.32) the postulate of antisymmetry of the many-electron system was not taken into account. The Pauli principle can be satisfied only in its **elementary form**, which says that in the product (6.32) above, all the one-electron states must be different and orthogonal, or rather because of spin, the spatial part of a pair of electrons can be the same, as they can be multiplied by the two possible eigenstates of S_z, as *H* is spin independent. This means that if we wish to determine the ground state of the *N* electron system we can choose those one-electron states in the product which belong to the lowest one-electron eigenvalues, where orbital and spin degeneracy must be taken into account, as well.

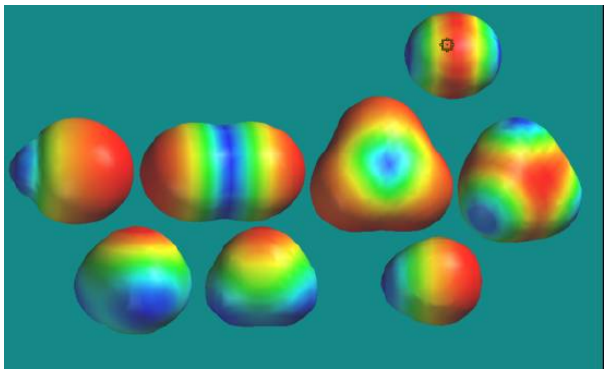


Figure 6.3: Electrostatic potential maps from Hartree-Fock calculations
http://science.csustan.edu/phillips/CHEM4610 Docs/CHEM4610_All Bonds Same.htm

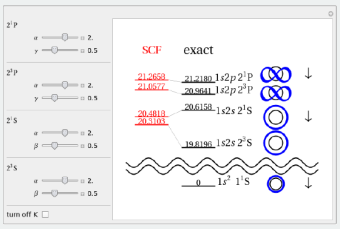
In spite of satisfying the Pauli principle in its elementary form (each electron is in a different one-particle state), it does not obey the real requirement, which states that the wave function of identical fermions must be antisymmetric. Therefore the (6.32) product of functions must be antisymmetrized. In order to do so one has to construct the Slater determinant (6.23) out of the *N* functions we have chosen, and calculate the potential energy from this multiparticle wave function. This improved method was proposed by V. Fock and J. Slater independently and it is called the Harterre Fock (HF) method. We only quote the resulting equation here:

$$\left(-\frac{\hbar^2}{2m}\Delta_i-\frac{Ze_0^2}{|\mathbf{r}_i|}+\sum_{j,jeqi}^{N}\int\frac{e_0^2|\varphi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i-\mathbf{r}_j|}d^3\mathbf{r}_j-\delta_{m_im_j}\sum_{j,jeqi}^{N}\int e_0^2\frac{\varphi_j(\mathbf{r}_j)\varphi_i(\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|}d^3\mathbf{r}_j\right)\varphi_i\left(\mathbf{r}_i\right)=\varepsilon_i\varphi_i\left(\mathbf{r}_i\right) \quad (6.38)$$

which is called the Hartree-Fock equation. It differs from the Hartree equation by the last term on the left hand side. Due to the Kronecker delta $\delta_{m_im_j}$ it is present only for electrons with identical spin projections. Here again the left hand side contains the φ-s of $k-1$-th step, while on the right hand side we have already ε_i and $\varphi_i(\mathbf{r}_i$ in the *k*-th step. It is to be repeated until self-consistency is achieved similarly to the case of the Hartree method, and it yields very good ground state energies and electronic densities for atoms.

We note that the HF method can be extended to calculate the electronic structure of molecules and solids. It is also worth to stress that there are many other approximate ways to find the electronic structure of atomic systems.

Animation



On this interactive animation we can investigate the lower excited states of a Helium atom. Besides the exact energy values results of SCF calculations is also shown. The SCF energy can be optimized by variation of some parameters which can be done by hand in the Demonstration. We can switch on and off the effect of exchange interaction to see how this interaction is responsible for the effect of the spin degrees of freedom.

http://demonstrations.wolfram.com/LowerExcitedStatesOfHeliumAtom/

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7: Molecular structure and spectra

Objectives

In this chapter we shall discuss the question about the internal structure and the energy of molecules, which depend not only on the distribution of the electrons like in atoms, but also on the location and motion of atomic nuclei. Although the different possible mechanisms responsible for the molecular spectra are interrelated, there are three kinds of motions that can be distinguished in practice, because the differences in their typical energies allow their characterization to be examined independently. The three main mechanisms determining the spectra of the molecules are their **electronic**, **vibrational** and **rotational** excitations.

Prerequisites

Chapters 2, 4-5-6. Molecules and valence in chemistry. Rotation of rigid bodies, the harmonic oscillator.

Introduction

For simplicity, and in order to grasp the essence of this topic, we shall consider diatomic molecules. In particular, the interaction between two neutral atoms and its dependence on their distance RR from each other will give us better insight into the nature of chemical bond. Also, the model of atomic orbitals, which gives an intuitive picture of the spatial electron distribution and plays an important role in chemistry, can be explained more readily for diatomic molecules. Since the energy levels of molecules are not only determined by electronic excitation but also by vibrations of the nuclei, or the rotation of the whole molecule around an axis through its centre of mass, the spectra of molecules are much more complex than those of atoms, but on the other hand they also give more detailed information about the internal structure and dynamics of molecules. First we come to the simplest discussion of the electronic states, and explain why two neutral atoms tend to form a molecule.

Molecular orbitals of diatomic molecules.

We shall consider a specific problem, the neutral H_2 molecule, where electron-electron interaction is also present, and this example explains also why two electrically neutral H atoms tend to form a stable molecule, instead of remaining separated. This is the long standing problem of valence, that can be explained only by quantum theory. In considering the H_2 molecule we shall assume in this section that the two protons are at **fixed positions** in space, and we will try to determine the two-electron wavefunction of the system in its ground state. The resulting energy will depend on the distance between the nuclei, and then the dynamics of that degree of freedom can be investigated further.

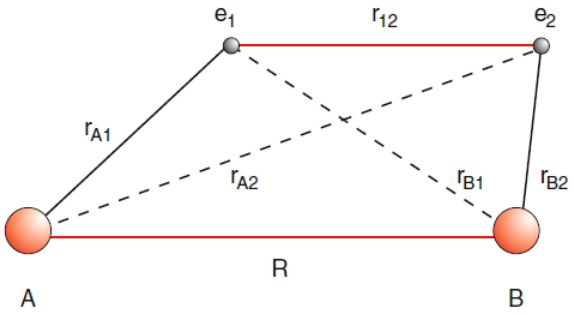


Figure 7.1: $\mathrm{H_2}$ molecule.

The Hamiltonian of the system, which does not contain nuclear motion (with $e_0^2 = q_0^2/4\pi\epsilon_0$) is

$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_A|} - \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_B|} - \frac{e_0^2}{|\mathbf{R}_2 - \mathbf{R}_A|} - \frac{e_0^2}{|\mathbf{R}_2 - \mathbf{R}_B|} + \frac{e_0^2}{|\mathbf{R}_1 - \mathbf{R}_2|} + \frac{e_0^2}{R} \qquad (7.1)$$

Problem 7.1

Explain the terms in this Hamiltonian.

One of the methods to find the energy eigenvalues is the following. We try to build a molecular wave function, called a molecular orbital as a linear combination of atomic orbitals, abbreviated as the MO LCAO method. Let us assume that in the ground state of the molecule the molecular orbital of one of the electrons can be written as the linear combination of normalized $1s$ ground state hydrogenic orbitals, which are centered at the nuclear positions:

$$\phi(\mathbf{r}) = c_A\phi_A(\mathbf{r}) + c_B\phi_B(\mathbf{r}) \quad (7.2)$$

where

$$\phi_A(\mathbf{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-(\mathbf{r}-\mathbf{R}_A)/a_0}, \quad \phi_B(\mathbf{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-(\mathbf{r}-\mathbf{R}_B)/a_0} \quad (7.3)$$

Due to the symmetry of the problem we choose $c_B = \pm c_A$ which leads after normalization to the following two wavefunctions for a single electron in the field of the two nuclei:

$$\phi_+(\mathbf{r}) = \frac{\phi_A(\mathbf{r})+\phi_B(\mathbf{r})}{\sqrt{2+2S(R)}} \quad \phi_-(\mathbf{r}) = \frac{\phi_A(\mathbf{r})-\phi_B(\mathbf{r})}{\sqrt{2-2S(R)}} \quad (7.4)$$

where $S(R) := \int \phi_A^*(\mathbf{r})\phi_B(\mathbf{r})d^3\mathbf{r}$ is a real constant, as the $1s$ functions above are real. $S(R)$ is called the overlap integral of the functions centred at the two nuclei. It will be a function of the distance $R = |\mathbf{R}_A - \mathbf{R}_B|$ between the nuclei, and it is diminishing with increasing R. Note that $\phi_+(\mathbf{r})$ in (7.4) is a symmetric while $\phi_-(\mathbf{r})$ is an antisymmetric function with respect to the exchange of the two identical nuclei. The question which of the two is to be used to describe the electrons will be discussed below, when also the electron spin is to be taken into account.

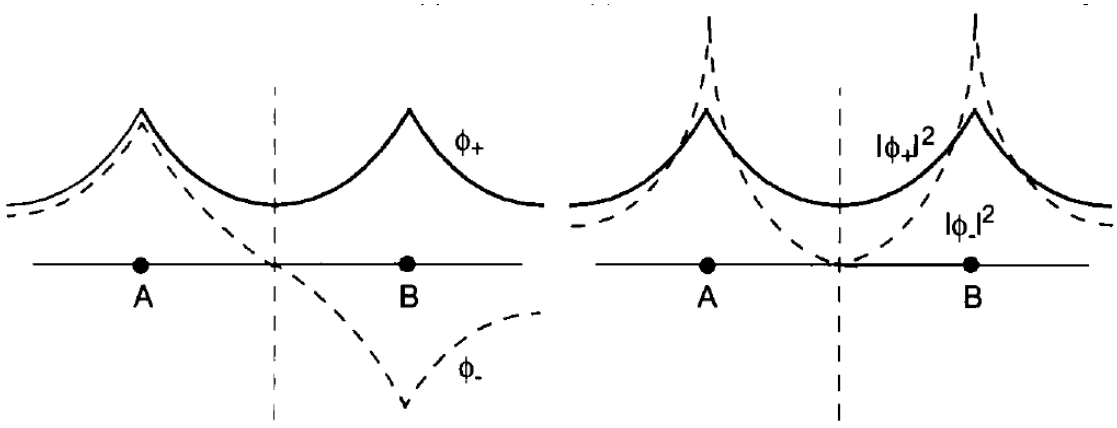


Figure 7.2: Wavefunctions and their absolute value square for a single electron in the field of the two nuclei. See Eqn.(7.4).

Now we assume that each of the two electrons is in one of the states $\phi_+(\mathbf{r})$, or $\phi_-(\mathbf{r})$ above, and look for the two-particle wave function as their product.

The singlet state

First we consider the possibility, when both of the electrons are in the $\phi_+(\mathbf{r})$ states:

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \phi_+(\mathbf{r}_1)\phi_+(\mathbf{r}_2) \quad (7.5)$$

Obviously this is symmetric with respect to the exchange of the two electrons, and therefore according to the postulate that requires the antisymmetry of the wave functions for fermions, it cannot be a true wave function. But as we know, this is not the total state, because the electrons possess a the spin degree of freedom, which – though not contained in the Hamiltonian – influences the symmetry properties of the state. We can complete the symmetric spatial wave function by an antisymmetric spin part by forming the Slater determinant:

$$\psi_s(\mathbf{r}_1, m_1, \mathbf{r}_2, m_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_+(\mathbf{r}_1)\chi^+(1) & \phi_+(\mathbf{r}_2)\chi^+(2) \\ \phi_+(\mathbf{r}_1)\chi^-(1) & \phi_+(\mathbf{r}_2)\chi^-(2) \end{vmatrix} \quad (7.6)$$

where $\chi^+(i)$ and $\chi^-(i)$ are the two different and orthogonal eigenstates of the S_z operator (spin up $+$, spin down $-$, according to the common usage (5.2)) for the *i*-th particle.

By expanding the determinant we get

$$\psi_s(\mathbf{r}_1, m_1, \mathbf{r}_2, m_2) = \frac{1}{\sqrt{2}}\phi_+(\mathbf{r}_1)\phi_+(\mathbf{r}_2)\left\{\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1)\right\} = \\ = \frac{1}{2\sqrt{1+S(R)}}\left\{\phi_A(\mathbf{r}_1) + \phi_B(\mathbf{r}_1)\right\}\left\{\phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_2)\right\}\left\{\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1)\right\} \tag{7.7}$$

In view of the last, spin dependent factor in (7.7) one sometimes simply says that in this state the two electrons have antiparallel spins. As the antisymmetric spin state $\left\{\chi^+(1)\chi^-(2) - \chi^+(2)\chi^-(1)\right\}/\sqrt{2}$ is called a **spin singlet**, the more correct statement is that the total ψ_s state is a spin singlet state.

The triplet state

From (7.4) we can also construct a spatial wave function which is antisymmetric with respect to the interchange of the electrons. In contrast to the symmetric ψ_s we take the combination

$$\psi_a(\mathbf{r}_1, \mathbf{r}_2) = \tfrac{1}{\sqrt{2}}\left\{\phi_+(\mathbf{r}_1)\phi_-(\mathbf{r}_2) - \phi_-(\mathbf{r}_1)\phi_+(\mathbf{r}_2)\right\} \tag{7.8}$$

which is antisymmetric if we change the electrons. This must be again completed by spin dependent parts, which must be then symmetric, so that the total state is antisymmetric. There are three different and orthogonal symmetric spin functions of the two particles, which are the following:

$$\chi^+(1)\chi^+(2), \quad \tfrac{1}{\sqrt{2}}\left\{\chi^+(1)\chi^-(2) + \chi^-(1)\chi^+(2)\right\}, \quad \chi^-(1)\chi^-(2) \tag{7.9}$$

Multiplying ψ_a with any of these we get again an allowed wave function $\psi_a(\mathbf{r}_1, m_1, \mathbf{r}_2, m_2)$. One loosely says, that the two spins are parallel in these states. As there are three of them, we call these three spin states, as well as the total wave function as a **triplet**.

Problem 7.3

Multiply ψa by the second of these symmetric spin states and write the result as a Slater determinant.

The energy expectation values of the states

One can now find the energies in the states ψ_s and ψ_a by calculating $\varepsilon_s = \int \psi_s^* H \psi_s d^3\mathbf{r}_1 d^3\mathbf{r}_2$ and $\varepsilon_a = \int \psi_a^* H \psi_a d^3\mathbf{r}_1 d^3\mathbf{r}_2$, where H is the Hamilton operator (7.1). In the calculations there appears the ground state energy ε_1 of an isolated H: $\frac{P_i^2}{2m} - \frac{e_0^2}{|R_i - R_{A(B)}|}$. In addition the result will contain the Coulomb energy

$$Q = \int \phi_A^2(\mathbf{r}_1)\phi_B^2(\mathbf{r}_2)\left(\frac{e_0^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e_0^2}{|\mathbf{r}_1 - R_B|} - \frac{e_0^2}{|\mathbf{r}_2 - R_A|}\right) d^3\mathbf{r}_1 d^3\mathbf{r}_2 + \frac{e_0^2}{R} \tag{7.10}$$

and the so called exchange energy *A*:

$$A = \int \phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)\phi_A(\mathbf{r}_2)\phi_B(\mathbf{r}_1)\left(\frac{e_0^2}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{e_0^2}{|\mathbf{r}_1 - R_B|} - \frac{e_0^2}{|\mathbf{r}_2 - R_A|}\right) d^3\mathbf{r}_1 d^3\mathbf{r}_2 + S^2(R)\frac{e_0^2}{R} \tag{7.11}$$

which is the measure of the overlap of the two electronic wave functions weighted by the potential energy, and results from the interplay of the Pauli principle and the Coulomb interaction. The result is

$$\varepsilon_s = 2\varepsilon_1 + \tfrac{Q+A}{1+S^2}, \quad \varepsilon_a = 2\varepsilon_1 + \tfrac{Q-A}{1-S^2} \tag{7.12}$$

Here both *Q* and *A* depend on the nuclear distance *R*. The Coulomb energy *Q* is positive, while apart from very small *R*-s *A* is negative and $|A| > Q$. This results in the dependence of the energy values of εsεs as shown in Fig. 7.3

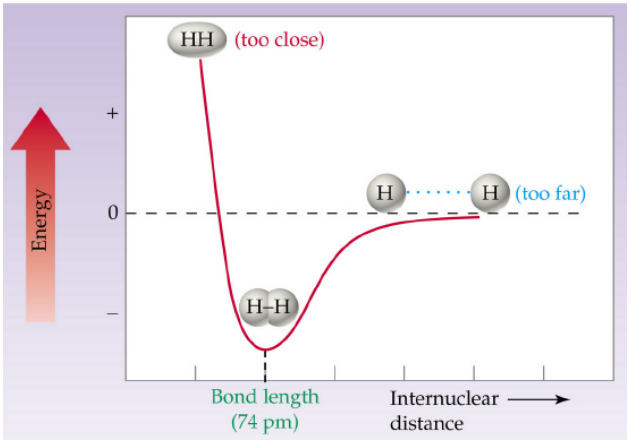


Figure 7.3: Dependence of the energy values of ε_s on the nuclear distance R.

This means that the singlet state (antiparallel spins in the sense of the last factor in (7.7)) is stable around an equilibrium distance $R = R_e$. The calculated value from this simple model is $R_e = 0.8\text{nm}$, while the measured value is 0.74nm. The state ψ_s is called therefore a **bonding state**, and it is denoted by σ. The other, triplet state, which is antisymmetric in space but the spins of the two electrons are parallel in the sense of (7.9) is not stable, there is no minimum in the energy, it is called an **antibonding** state, and it is denoted by σ^*. See figure 7.4 and the animation below.

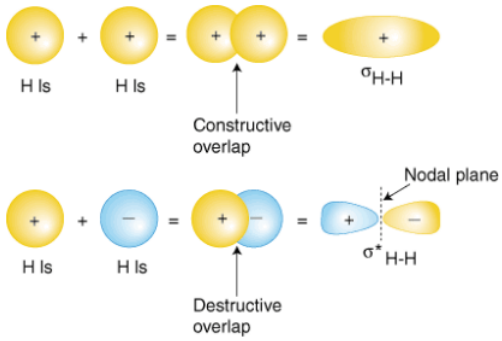
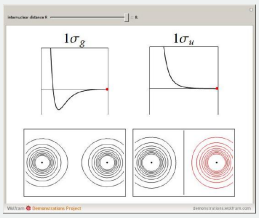


Figure 7.4: Schematic drawing of bonding and antibonding states.
http://www.sparknotes.com/chemistry/bonding/molecularorbital/section1.rhtml

Note



The lowest-energy bonding and antibonding molecular orbitals (MO) for a homonuclear diatomic molecule are shown, as the internuclear distance is varied. The red contours designate negative values of the wavefunction.

http://demonstrations.wolfram.com/BondingAndAntibondingMolecularOrbitals/

The H_2 molecule is a **homonuclear** diatomic molecule, where homonuclear means that the two nuclei are identical. In some of the heteronuclear diatomic molecules (different atoms) there is another effect besides the one we discussed here. In HCl for instance the electron cloud will be asymmetric along the molecular axis, the electron from the H atom tends to get closer to the Cl and simply the attraction of the proton by the negatively charged Cl ion will stabilize this molecule.

The example we considered above was one of the simplest ones. The calculation of the **electronic structure** of very complicated large molecules have become possible in the second half of the 20th century due to the technical development of fast electronic

computers, as well as to the evolution of sophisticated algorithms and program packages, which are the subject of the science called quantum chemistry.

Molecular spectra

In the atomic system, our consideration of radiative transitions was limited to the problem of electronic transitions between states. In the molecules, the internal structure allows also for transitions involving **rotational and vibrational excitations** of the constituent nuclei. As with atoms, electronic transitions are typically of the order of eV, corresponding to wavelengths in or near the optical region. However, it is unlikely that an electronic transition will occur without inducing motion of the nuclei, as well, because the equilibrium distances between the nuclei will be different in the initial and final electron states. The typical energies of rotational states of molecules are much smaller than those of electronic excited states, of order $\hbar^2/2\Theta$, where Θ is the molecular moment of inertia. Substituting typical values for the interatomic spacing and atomic masses, one finds that rotational energies are of the order of $10^{-4}\mathrm{eV}$ corresponding to the far infra-red or microwave regions. Typical energies for vibrational excitations of molecules are around $10^{-1}\,\mathrm{eV}$ corresponding to the infra-red waveband. All of these types of transitions can occur radiatively, i.e. through the emission or absorption of a photon of the appropriate frequency $\nu = \Delta\varepsilon/h$. As in the case of atoms, the most probable radiative transitions are usually electric dipole transitions. In an electric dipole transition, the photon carries away or brings in one unit of angular momentum and negative parity, so there will be the usual selection rule for the change in the total angular momentum quantum number of the molecule: $\Delta J = 0, \pm 1$, but not $0 \to 0$, accompanied by a change in the parity of the molecular state (which may impose further restrictions on ΔJ).

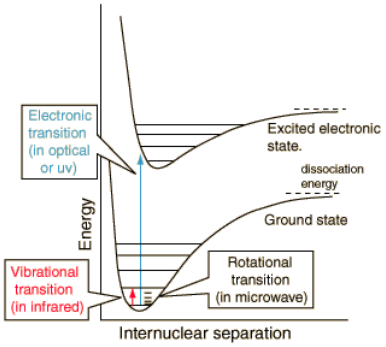
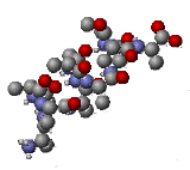


Figure 7.5: This figure visualizes the difference in orders of magnitude for the different type of transitions (electronic, vibrational and rotational).
http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/molec.html

In a gas or a liquid, transitions can also be produced by collisions between their molecules. The appropriate energy change can be provided by excitation or de-excitation of the other molecule, or as part of the kinetic energy of the collision. Such non-radiative transitions do not have to obey the selection rules above. Thus, for example, a molecule in a metastable state, i.e. one that cannot return to the ground state via an allowed radiative transition, can be de-excited by a collision. In the absence of any incident radiation or other non-thermal sources of excitation, collisions will bring about a thermal distribution of molecular energy levels, with the number of molecules in state ii being given by , where g_i is the degeneracy and ε_i the energy. At room temperature $k_B T = 2 \times 10^{-2}\mathrm{eV}$, so typically many rotational states of molecules are excited, but not electronic or vibrational.

In a rotating and vibrating molecule the kinetic energy of the nuclei is small compared to the energy of the molecular state. This is because the nuclear masses are large, and therefore their motion is slow compared to the motion of the electrons. This allows the separation of the total wave function $\Phi(\mathbf{R},\mathbf{r})$ into a product $\Phi(\mathbf{R},\mathbf{r}) = \phi(\mathbf{R})\psi(\mathbf{R},\mathbf{r})$ of a nuclear wave function $\phi(\mathbf{R})$ and an electronic function $\psi(\mathbf{R},\mathbf{r})$ which depends on the electron coordinates $\mathbf{r}$ and contains the nuclear positions $\mathbf{R}$ as parameters. This approximation is called the adiabatic or Born-Oppenheimer approximation. Within this approximation the total energy of a molecular level can be written as a sum of the electronic, vibrational and rotational energies.

Animation



Shown here is the thermal motion of a segment of protein alpha helix. Molecules have various internal vibrational and rotational degrees of freedom. This is because molecules are complex objects; they are a population of atoms that can move about within a molecule in different ways. This makes molecules distinct from the noble gases such as helium and argon, which are monatomic (consisting of individual atoms).

http://upload.wikimedia.org/Wikipedia/commons/2/23/Thermally_Agitated_Molecule.gif

Molecular rotation

The model of a rigid diatomic molecule

In general, the Schrödinger equation for the nuclear motion has many solutions, which give the various molecular energy levels for a given electronic configuration. The simplest case is that of a diatomic molecule where the molecule can be characterized by its moment of inertia with respect to its centre of mass. If we assume in the first approximation that the molecule is rigid, and we consider the problem in the system fixed to the centre of mass of the molecule, then the translational kinetic energy can be separated. From the point of view of rotations, the molecule is characterized by its moment of inertia $\Theta = \mu r_0^2$ about an axis through the centre of mass orthogonal to the bond, where r_0 is the equilibrium bond length, and μ is the reduced mass of the two atoms. The rotational kinetic energy can be expressed by the angular momentum $\mathcal{L} = \Theta\omega$ as

$$\tfrac{1}{2}\Theta\omega^2 = \tfrac{\mathcal{L}^2}{2\Theta} \quad (7.13)$$

and if we replace the classical $\mathcal{L}$ by the operator of the angular momentum we get the Hamilton operator of the pure rotational motion:

$$H = \tfrac{L^2}{2\Theta} \quad (7.14)$$

The stationary states are the solutions of the eigenvalue equation

$$\tfrac{L^2}{2\Theta}\Phi = \varepsilon_J \Phi \quad (7.15)$$

As L^2 is a square of an angular momentum belonging to an orbital motion its eigenvalues are of the form $\hbar^2 J(J+1)$, (in molecular spectroscopy instead of the notation ℓ, we use J) where $J = 0, 1, \ldots$, and its projection m_J takes the values $J, J-1, \ldots, -J$). The rotational energy eigenvalues are therefore

$$\varepsilon_J = \tfrac{\hbar^2}{2\Theta} J(J+1) \quad (7.16)$$

while the eigenfunctions will be the spherical harmonic functions $\Phi = Y_J^{m_J}$. As mentioned earlier, the typical energies of rotational states of molecules are much smaller than those of electronic excited states. Since molecular dimensions are determined by the electronic wavefunction, their scale is set by the Bohr radius a_0. Thus moments of inertia are of order $m_N a_0^2$ and the scale of rotational energies is $\hbar^2/m_N a_0^2$. For the electronic states, the Heisenberg inequality implies momenta of order $\hbar/a_0$ and hence electron energies around $\hbar^2/\left(m_e a_0^2\right)$, a factor of $m_N/m_e \simeq 10^4$ greater. To bring about a radiative rotational transition, an emitted or absorbed photon must interact with the electric dipole moment of the molecule. In a pure rotational transition the initial and final electronic states are the same, therefore the state needs to have a permanent electric dipole moment. Thus we can have purely rotational radiative transitions in heteronuclear diatomic molecules like HCl and CO, which have permanent dipole moments, but not in homonuclear ones like H_2 and O_2.

The usual electric dipole selection rules apply: $\Delta J = \pm 1, 0$ with a parity change. In a rotational state with angular momentum quantum numbers J and m_J, the nuclear wavefunction is proportional to the spherical harmonic $Y_J^{m_J}$, which has parity $(-1)^J$. (For simplicity, we consider only molecular states in which the electronic wavefunction has zero angular momentum and even parity). Then the fact that the parity must change in a radiative transition excludes the possibility $\Delta J = 0$. Therefore the possible energy changes in emission ($J+1 \longrightarrow J; J = 0, 1, 2 \ldots$) are given by:

$$\Delta\varepsilon = \tfrac{\hbar^2}{2\Theta}[(J+1)(J+2) - J(J+1)] = \tfrac{\hbar^2}{\Theta}(J+1) \quad (7.17)$$

Accordingly the spectrum is expected to consist of lines with increasing frequencies.

To specify a spectral line in practical molecular spectroscopy one uses the wavenumber $\bar{\nu} = 1/\lambda = \nu/c$, which is obtained according the Bohr rule ($\bar{\nu} = \Delta\varepsilon/hc$) as a difference of terms:

$$F_J = \frac{\varepsilon_J}{hc} \quad (7.18)$$

Here the word **term** is the standard terminology for the expression in (7.18). So the wavenumbers corresponding to the energy differences, i. e. to the transition, are obtained from (7.17) as:

$$\bar{\nu}_{\mathrm{rot}}(J) = 2B(J+1) \quad (7.19)$$

where the **rotational constant** $B = \hbar/4\pi c\mu R_e^2$, is expressed here with the reduced mass μ. Rotational transitions fall into the THz-GHz domain, i.e. in the far infrared or microwave range. In fact, the rate for spontaneous emission between rotational states is very small, because of the small energy release. The spontaneous emission rate varies as ω^3, and so rotational transitions are more conveniently studied by absorption spectroscopy. The same formula for the transition energies clearly applies to the $J \longrightarrow (J+1)$ absorption case, as well. Observation of this spacing can be used to determine the moment of inertia and hence the bond length of the molecule.

The intensities of rotational spectral lines show some interesting features. Although the transition matrix element depends on the quantum numbers, the dominant factor is usually the population of the initial state. As mentioned earlier, non-radiative transitions due to molecular collisions bring about a thermal distribution,

(7.20)

This increases with J up to some value, which depends on the temperature, and then decreases. Thus successive spectral lines increase and then decrease in intensity.

Centrifugal Distortion

A real molecule is not rigid. When it rotates, the centrifugal force acts on the atoms and the internuclear distance increases to a value *R* where this force $F_c = -M\omega^2 R$ is compensated by the restoring force $F_r = -dE_{pot}(R)/dR$ holding the two atoms together, which depends on the slope of the potential energy function $E_{pot}(R)$. In the vicinity of the equilibrium distance R_e the potential can be approximated by a parabolic function. This leads to a linear restoring force

$$F_r = -k\,(R - R_e) \quad (7.21)$$

From the relation $J^2 = \Theta^2\omega^2 = M^2R^4\omega^2$ we obtain:

$$M\omega^2 R = \frac{J(J+1)}{MR^3}\hbar^2 = k\,(R - R_e) \quad (7.22)$$

which leads to

$$R = R_e + \frac{J(J+1)\hbar^2}{MkR^3} \quad (7.23)$$

This means that the internuclear distance *R* is increased by the molecular rotation. Since the potential energy $E_{pot}(R)$ has a minimum for $R = R_e$, in case of $ReqR_e$ we have an additional energy $\Delta E_{pot} = \frac{k}{2}(R - R_e)^{\,2}$ in the case of a nonrigid rotor. The total energy of the nonrigid rotor is then

$$\varepsilon_{rot} = \frac{J(J+1)\hbar^2}{MR^2} + \frac{1}{2}k(R - R_e)^{\,2} \quad (7.24)$$

If we express RR on the right side of (7.23) by R_e and *k* with the help of (7.22) we obtain

$$R = R_e\left(1 + \frac{J(J+1)\hbar^2}{MkR_e^4}\right) \quad (7.25)$$

where the second term is $\ll 1$. This allows us to expand $1/R^2$ into the power series

$$\frac{1}{R^2} = \frac{1}{R_e^2}\left(1 - \frac{2J(J+1)\hbar^2}{MkR_e^4} + \frac{3J^2(J+1)^2\hbar^4}{M^2k^2R_e^8} \mp \ldots\right) \quad (7.26)$$

and the rotational energy becomes up to third order in $\hbar^2$

$$\varepsilon_{rot} = \frac{J(J+1)\hbar^2}{2MR_e^2} - \frac{J^2(J+1)^2\hbar^4}{2M^2kR_e^6} + \frac{3J^3(J+1)^3\hbar^6}{2M^3k^2R_e^{10}} \quad (7.27)$$

This means that for a given value of the rotational quantum number J the centrifugal force makes the moment of inertia larger and therefore the rotational energy smaller. This effect overcompensates the increase in potential energy.

Using the term-values again instead of the energies, (7.27) becomes

$$F_{rot}(J) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 \quad (7.28)$$

with the rotational constants:

\(\F_{r o t}(J)=B_{e} J(J+1)-D_{e} J^{2}(J+1)^{2}+H_{e} J^{3}(J+1)^{3}) (7.29)

The experimental spectroscopic accuracy is nowadays sufficiently high to measure even the higher order constant H_e.

Vibrational transitions

Harmonic approximation

Another important type of molecular motion is vibration, in which the nuclei oscillate around their equilibrium positions. For a diatomic molecule, we can make a Taylor expansion of the molecular potential $E_0(R)$ around the equilibrium nuclear separation R_0 to obtain

$$E_0(R) = E_0(R_0) + \tfrac{1}{2}(R-R_0)^2 \frac{\partial^2}{\partial R^2} E_0(R)\Big|_{R=R_0} + \ldots \quad (7.30)$$

The first derivative vanishes, because $E_0(R)$ has a minimum at R_0. $E_0(R_0)$ is a constant, and the second term on the right-hand side can be written as , which is the potential for a simple linear harmonic oscillator with $X = R - R_0$, and classical frequency

$$\omega = \left[\frac{1}{\mu}\frac{\partial^2}{\partial R^2} E_0\Big|_{R=R_0}\right]^{1/2} \quad (7.31)$$

where μ is the reduced mass. According to the quantum theory of the harmonic oscillator the energy levels including nuclear vibration is given by

$$\varepsilon(v) = E_0(R_0) + \hbar\omega(v+1/2), \quad v = 0, 1, 2 \ldots \quad (7.32)$$

The excitation energies of molecular vibrational states are typically larger than those of rotational states by a factor of about $(m_N/m_e)^{1/2}$ and smaller than electronic excitation energies by a factor of about $(m_e/m_N)^{1/2}$. As we discussed earlier, $E_0(R_0)$ will be of the same order of magnitude as atomic energies, i.e. of the order of $\hbar^2/m_e a_0^2$, where a_0 is the Bohr radius. Thus, on dimensional grounds, $\partial_R^2 E_0\big|_{R_0}$ will be of order $\hbar^2/m_e a_0^4$, and $\hbar\omega \sim \hbar^2/\sqrt{m_e m_N}\, a_0^2$. Therefore the vibrational energy is smaller than the electronic by a factor of order $\sqrt{m_e/m_N}$. This puts vibrational spectra in the wavelength region around 10μm, which is in the infra-red.

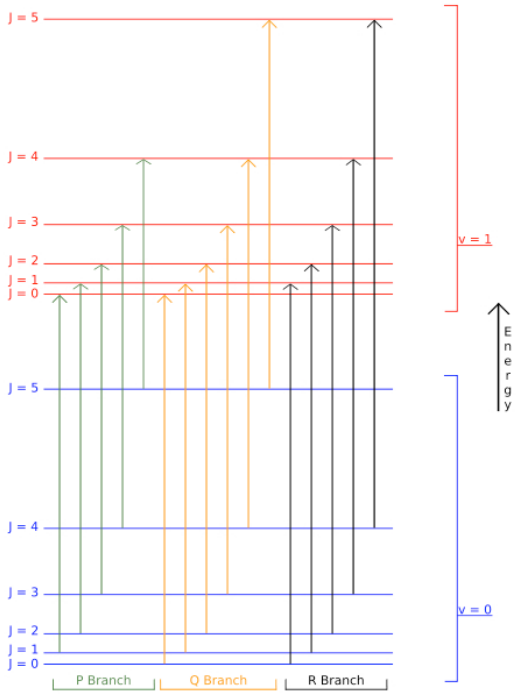


Figure 7.6: Generally vibrational transitions occur in conjunction with rotational transitions. Consequently, it is possible to observe both rotational and vibrational transitions in the vibrational spectrum. The top figure shows an energy level diagram demonstrating some of the transitions involved in the IR vibrational-rotational spectrum of a linear molecule: P branch (where $\Delta J = -1$), Q branch (not always allowed, $\Delta J = 0$) and R branch ($\Delta J = +1$).
http://en.Wikipedia.org/wiki/File:Vibrationrotationenergy.svg

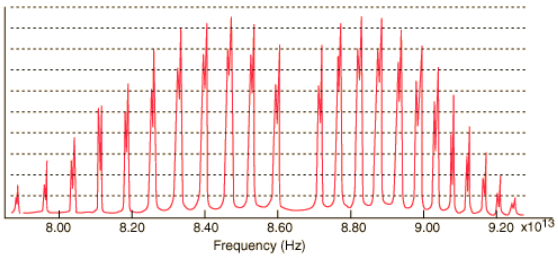


Figure 7.7: The vibration-rotation spectrum of HCl. The left hand branch of the spectrum represents the P branch and the right the R. The Q branch is not allowed. The splitting of the lines is associated with the two isotopes ^{35}Cl and ^{37}Cl.

We can now check explicitly that the Born-Oppenheimer approximation is valid for nuclear vibrational states, as follows. The mean **square** nuclear vibrational momentum is of order $m_N\hbar\omega \sim \sqrt{m_N/m_e}(\hbar/a_0)^2$, which means that $\nabla_N^2\phi_k \sim \sqrt{m_N/m_e}\phi_k/a_0^2$, where ϕ_k is the nuclear part of the wavefunction. On the other hand $\nabla_N^2\psi \sim \psi/a_0^2$, where ψ is the electronic part. Thus $\phi\nabla_N^2\psi$ is smaller than $\psi\nabla_N^2\phi$ by a factor of $\sqrt{m_e/m_N}$, and it is legitimate to neglect the former.

For vibrational transitions we have the selection rule $\Delta v = \pm 1$. This implies only a single energy in the spectrum

$$\Delta\varepsilon = (\varepsilon_{v+1} - \varepsilon_v) = \hbar\omega \quad (7.33)$$

corresponding to the classical frequency of oscillation.

Anharmonic effects

In practice the Taylor expansion around $R = R_0$ has non-negligible terms of higher than second order and the harmonic oscillator approximation is not very reliable: there is anharmonicity. The flattening of the molecular potential energy curve at larger separations has the effect of bringing the energy levels closer together. Thus transitions at larger vv have lower energies than that given above. Also, since the true stationary state wavefunctions are not precisely harmonic oscillator eigenfunctions, our selection rule is not exactly valid, and transitions with $|v| > 1$ become possible. A good approximation of the potential that includes anharmonic effects is the so called Morse potential having the form:

$$E_0(R) = D_e\left(1 - e^{-a(R-R_e)}\right)^2 \quad (7.34)$$

where D_e is the dissociation energy, the limit to which the potential converges at $R \to \infty$. The minimum of the potential is at the equilibrium value R_e of the distance between the atoms. The definition in (7.31) yields:

$$\omega = a\sqrt{2D_e/\mu} \quad (7.35)$$

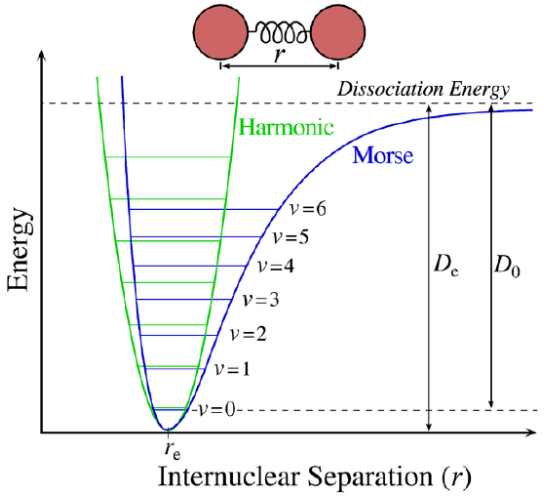


Figure 7.8: The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by |(ħω\), the Morse potential level spacing decreases as the energy approaches the dissociation energy.
http://en.Wikipedia.org/wiki/File:Morse-potential.png

The eigenvalue equation of the corresponding vibrational Hamiltonian $\frac{P^2}{2\mu} + D_e\left(1 - e^{-a(R-Re)}\right)^2$ in one dimension can be solved in closed form yielding the exact eigenvalues:

$$\varepsilon(v) = E_0\left(R_0\right) + \hbar\omega\left(v + \tfrac{1}{2}\right) - \tfrac{\hbar^2\omega^2}{4D_e}\left(v + \tfrac{1}{2}\right)^2, \quad v = 0, 1, 2\ldots \quad (7.36)$$

This provides the energy separation

$$\Delta\varepsilon(v) = \hbar\omega\left(1 - \tfrac{\hbar\omega}{2D_e}(v+1)\right) \quad (7.37)$$

which means that the transition frequencies are decreasing, with increasing vibrational quantum numbers. In contrast to the harmonic case the number of bound states is finite $[s]+1$, where $s = \frac{\sqrt{2\mu D_e}}{\hbar\alpha} - 1/2$, and $[s]$ denotes the integer part of s.

Vibrational modes for polyatomic molecules can be quite complicated. If there are N atoms, in general there are $3N-6$ normal modes ($3N$ coordinates minus 3 to define the overall position of the centre of mass, and minus 3 to define the overall orientation of the molecule) or $3N-5$ in the case of a diatomic molecule. Thus, in the simple case of the linear CO_2 molecule, there are four modes, two with the atoms remaining collinear (one with the two O atoms moving in antiphase with the C stationary, and one with the O atoms moving in phase in the opposite direction to the C atom) and two degenerate orthogonal bending modes. The more detailed classification of the possible vibrational modes of polyatomic molecules relies strongly on their symmetry properties and needs the mathematical method called group theory.

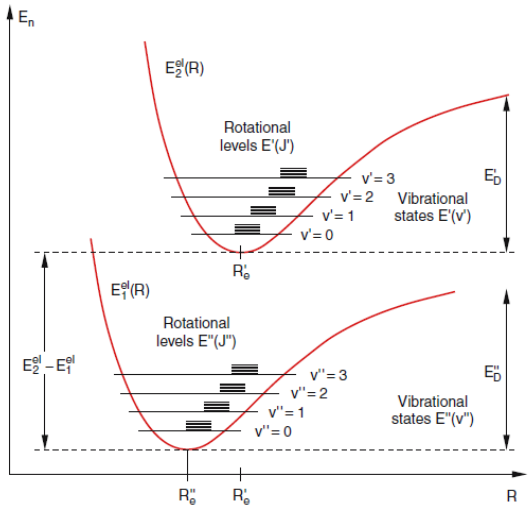


Figure 7.9: The combined electronic vibrational and rotational levels of a molecule. We see that the largest energy difference is between the electronic states. The electronic spectrum consists of a system of vibrational bands, while each vibrational band includes many rotational lines.

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8: Bose Einstein Condensation

Objectives

In Chapter 6 we have already discussed the microscopic many body description of a Bose condensate. In this chapter we focus on the experimental realization of this very specific, interesting and fundamental kind of matter. And we give some insight into its genuinely quantum mechanical characteristics.

Prerequisites

De Broglie's hypothesis from Chapter 1. Particles with spin in magnetic fields from Chapter 5. The material on bosons in Chapter 6.

Introduction

The Bose-Einstein condensate (BEC) is a very specific, interesting and fundamental kind of matter, actually a gas, consisting of atomic particles. It shows up two different genuinely quantum mechanical characteristics simultaneously. One of them is **the wave like nature of massive atoms, a behaviour becoming more and more explicit at very low temperatures**. The other property is that **particles with integer intrinsic angular momentum (spin) can in principle all be in the same quantum state**. Photons, the quanta of electromagnetic radiation are specific kind of bosons of spin 1, while their rest mass is zero. Satendyra Bose derived Planck's law by assuming this property, and sent his work to Einstein in 1924, who – recognizing the importance of the idea – recommended the publication of the paper of Bose. Soon after this, in the same year Einstein himself discovered that the derivation can be extended to the case when the gas consists of **massive particles** (unlike photons) and predicted that an ordinary gas can also be brought in that specific state, that is why it got the name Bose-Einstein condensate. As we said, only particles with integer spin may form a condensate, and such particles are called bosons, in honour of Bose. Electrons and other particles with half integer spin do not show up this behaviour, unless a specific interaction couples them to pairs, so that the pair has integer spin. We come to this point below.

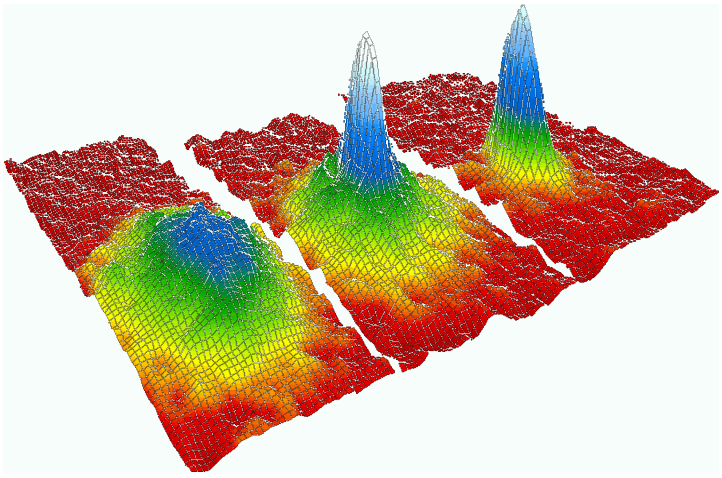


Figure 8.1: Cooling rubidium atoms to less than 170 billionths of a degree above absolute zero caused the individual atoms to condense into a "superatom" behaving as a single entity. The graphic shows three-dimensional successive snap shots in time in which the atoms condensed from less dense red, yellow and green areas into very dense blue to white areas.
http://en.Wikipedia.org/wiki/Bose_Einstein_condensate

Further Reading

Predicted 1924 …Created 1995. Check out the BEC Homepage for introductory level lessons on BEC with animations, explaining the physics behind.
http://www.colorado.edu/physics/2000/bec/

In chapter 6 we have already discussed the microscopic many body description of a Bose condensate. We repeat it here shortly: The independent particles are all in their identical lowest energy one particle state, i.e. in their ground state. The corresponding total wave function is:

$$\Psi_0\left(\xi_1,\xi_2,\ldots,\xi_N\right)=\varphi_0\left(\xi_1\right)\varphi_0\left(\xi_2\right)\ldots\varphi_0\left(\xi_N\right) \quad (8.1)$$

In spite of its name a Bose-Einstein condensate is a **dilute ideal, or almost ideal gas**. While in air e.g. at atmospheric pressures and room temperatures the number of molecules (N_2 and O_2) in $1\mathrm{cm}^3$ is 10^{19}, in a condensate the density is only $10^{12}-10^{13}$ atoms $/\mathrm{cm}^3$. In fluids and in solids this concentration is 10^{22} atoms $/\mathrm{cm}^3$ whilst in atomic nuclei the nucleon density is 10^{38} particles $/\mathrm{cm}^3$. Nevertheless at very low temperatures the condensate has very different properties from an ordinary ideal gas. The energy spectrum of the gas is practically continuous, so the excitations are of very low energy, which means that an ultralow temperature is necessary to achieve even the vicinity of the required ground state.

In the present chapter we come to the practical side of the problem and discuss the possibilities of the creation of this state of matter. The most important characteristic is that at appropriately low temperatures atoms lose their individuality and show collective behaviour. We can find the condition when this happens by a relatively simple calculation. The momentum p of the atoms is connected with their de-Broglie wavelength by the formula:

$$p=mv=h/\lambda_{dB}, \quad \text{or} \quad \lambda_{dB}=h/mv \quad (8.2)$$

The velocity depends on the temperature, or more precisely, thinking of the classical **ideal gas**, we have from the equipartition theorem the equation $mv^2/2=3k_BT/2$, where ν is the average velocity of the particles, and k_B is the Boltzmann constant. Then we get the momentum and the thermal de Broglie wavelength according to:

$$v=\sqrt{\tfrac{3k_BT}{m}}, \quad p=mv=\sqrt{3k_BTm} \quad (8.3)$$

$$\lambda_{dB}=\tfrac{h}{p}=\tfrac{h}{\sqrt{3k_BTm}} \quad (8.4)$$

This latter length scale is where the wave-like properties of the particles do manifest. At room temperatures this length is very small, but it increases with lowering the absolute temperature. If we consider a particle in a vessel of volume V containing N_0 atoms, the density of the particles is $n=N_0/V$, and its inverse is the volume shared by a single particle on the average: $V/N_0=n^{-1}$. The linear size of a corresponding cube is $n^{-1/3}=\sqrt[3]{V/N_0}$. Assume that by cooling the gas we can achieve a λ_T which is of the order of the distance between the particles $n^{-1/3}$. At this value of the temperature we expect that the individuality of the particles is lost, and collective quantum mechanical phenomena appear. The condition of this, with the above simple reasoning is the fulfillment of the inequality

$$n^{1/3}\lambda_T=n^{1/3}\tfrac{h}{\sqrt{3kTm}}\gtrsim 1 \quad (8.5)$$

In order to get such a gas there seem to be two possibilities. One of them is to increase *n*, i.e. the density of the atoms. But a simple calculation shows that at milikelvin temperatures, attainable with traditional cooling technologies this would mean a density $n=10^{28}\mathrm{m}^{-3}$ which is the density of a fluid or a solid. Therefore the sample would be very far from an ideal gas, like the Bose condensate, which assumes that there is no direct interaction between the particles. So the effect will certainly be masked by the strong interaction between the constituent particles.

Problem 8.1

Calculate the number density (concentration) of the H gas and a $^{23}_{11}\mathrm{Na}$ gas at $0^\circ\mathrm{C}$ and atmospheric pressure. Use the universal gas law. For an atomic gas of Hydrogen the mass of a single atom is essentially that of the proton, $1.66\times10^{-27}\mathrm{kg}$, the mass of the $^{23}_{11}\mathrm{Na}$ atom is about 23 times larger $3.8\times10^{-27}\mathrm{kg}$.

There is one exception, where there is some remnant trace of the quantum effect following from the Bose statistics, and this is the isotope $^4_2\mathrm{He}$. This material becomes a fluid at $4.2\mathrm{K}$ at normal pressures, so by no means can it be considered to be an ideal gas. Still, when cooling it further, below $2.18\mathrm{K}$ it shows strange properties, the most surprising of which is superfluidity. The effect was discovered in 1937 by Pyotr Kapitsa in Moscow, and by John Allen and his co-worker Don Misener in Cambridge (England). In the case of He the mass mm is relatively small, which according to (8.5) shows that in this material the unusual properties could be connected with Bose-Einstein condensation. This was first suggested by Fritz London in 1938. By the middle of the 20th century it became widely accepted among physicists that the very complicated phase transition of He at $2.18\mathrm{K}$ is a kind of a Bose-Einstein

condensation, which however does not appear in its clean form, because it is veiled by the weak, but still existing interaction between the atoms of He.

Problem 8.2

Is it possible in principle to observe Bose Einstein condensation in Hydrogen? Why is that liquid He shows a somewhat related effect, while H, which is 4 times lighter is not a superfluid?

As we have noted Bose condensation appears only for bosons which have integer spin. However at even lower temperatures fermions can also form specific kinds of a condensates. A necessary condition for this is the formation of pairs: a pair of fermions is a boson, as the spin of the pair is then an integer. This is the reason of superconductivity, where a pair of electrons, called a Cooper pair is formed, and the effect of superconductivity can be considered to be a kind of superfluidity of these pairs. In the case of superconductivity the weak attractive force between the electrons is created indirectly through their interaction with the motion of the ions of the crystal lattice. J. Bardeen, L. Cooper and R. Schrieffer won the Nobel prize in 1972 for their microscopic explanation of superconductivity in 1957.

Further Reading

Under this link you can fin the details of the 1972 Nobel Prize in Physics won by John Bardeen, Leon N. Cooper and Robert Schrieffer for their microscopic explanation of superconductivity.
http://www.nobelprize.org/nobel_prizes/physics/laureates/1972/

Another example is the isotope $^3_2$He, which is a fermion, having only one neutron in its nucleus instead of two as in $^4_2$He. It was observed that $^3_2$He also shows superfluidity below at $2.5\mathrm{mK}$, which is three orders of magnitude lower than that of its bosonic variant. Here again these atoms may form pairs at these very low temperatures which is necessary for the stability of the very weak coupling of the pair. D. Lee, D. Osheroff and R. C. Richardson won the 1996 Nobel Prize in Physics for their discovery this effect, and A. Legget in 2003 for its theoretical explanation.

Further Reading

Under this link you can fin the details of the 1996 Nobel Prize in Physics won by D. Lee, D. Osheroff and R. C. Richardson for their or their discovery of superfluidity in helium-3.
http://www.nobelprize.org/nobel_prizes/physics/laureates/1996/

Further Reading

Under this link you can fin the details of the 2003 Nobel Prize in Physics won by Alexei A. Abrikosov, Vitaly L. Ginzburg and Anthony J. Leggett for their pioneering contributions to the theory of superconductors and superfluids.
http://www.nobelprize.org/nobel_prizes/physics/laureates/2003/

Atoms that can exhibit BE Condensation

A simple rule to decide if an ordinary atom is a fermion or a boson is to count the number of its elementary fermion constituents. The spin of all atomic constituents (electrons, protons, neutrons) is half integer so if the number of the nuclei+electrons is even then the atom is a boson. If this number is odd then the atom is a fermion. (We note here in addition, that at a more elementary level the spin $1/2$ of the nucleons is a result of adding the spins of the three quarks each possessing a spin value $1/2$.)

So one of the candidates that seemed appropriate to create a condensate was the gas of $^{23}_{11}\mathrm{Na}$ atoms. It has 11 electrons, 11 protons and 12 neutrons so their spin must add up to an integer. In addition, due to the large transition dipole moment of the Na D line (doublet) of the transition around 589 nm, it can be effectively manipulated by optical methods.

In more detail: 10 of the electrons of this atom form a closed configuration filling the $n=1$ and $n=2$ shells, similar to the 10 electrons of Ne, and resulting in zero spin. The 11-th electron of spin $s=1/2$ causes the half integer spin of the electron cloud of Na, resulting in the $3^2S_{1/2}$ state. This symbol – as usual – corresponds to the notation $n^{2s+1}L_j$ meaning that the highest energy electron is on a shell with principal quantum number $n=3$, the spin multiplicity is $2s+1=2$, the orbital angular momentum of the valence electrons is a state with $L=0$, i.e a centrally symmetric SS state, the total angular momentum is $J=1/2$ that comes from $J=L+S$. The 23 nucleons (11 protons + 12 neutrons) in its nucleus, has each a spin of 1/2. As 23 is an odd number the nuclear spin must add up to a half integer, and its value is actually $I=3/2$. It turns out that the **total spin** of the atom is either $F=1$ resulting from $|I-J|$ or $F=2$, resulting from $I+J$. So the total spin is an integer, the $^{23}_{11}\mathrm{Na}$ atoms are bosons.

Problem 8.3

Which of the two isotopes of $^{6}_{3}\mathrm{Li}$ and $^{7}_{3}\mathrm{Li}$ is a boson and which is a fermion?

Experimental observation of BEC

The main task is to achieve the low temperature necessary for the formation of a condensate. The first step is optical or Doppler cooling of the atoms with light.

Assume that a light of frequency $\nu=\omega/2\pi=c/\lambda$ is shone on a gas of atoms that is on resonance with one of the atomic transitions. The photons have energy $\hbar\omega$ and a momentum $2\pi\hbar/\lambda=\hbar k$. The atom of mass mm absorbing a photon will have a different velocity it had before the absorption, because of momentum conservation. If the atom has a momentum opposite to the one of the photon, i.e. they move into opposite directions, then after absorption the velocity of the atom will be smaller by the very small value $\hbar k/m=h\nu/mc$ because

$$m\nu'=m\nu-\hbar k \quad (8.6)$$

But atoms moving in the opposite direction as the photon absorb at frequencies $\omega=\omega_0-kv$.

The atom absorbs the energy $\hbar\omega$, gets excited, and soon after emits again the photon, which causes a recoil again. But the direction of the emitted photon is randomly distributed in the whole 4π solid angle. If the atom undergoes many cycles of absorption and emission during its interaction with the laser beam, the time average over the momentum obtained during emission will be zero while the one obtained in the absorption process is always negative, at least for the atoms moving opposite to the laser beam. Therefore the net result is a loss of momentum and a loss of kinetic energy of the atoms, which means that the temperature of the gas as a whole will be lower. It can be shown by formal mathematical arguments that the effect of Doppler cooling can be expressed as a velocity dependent friction force

$$\mathbf{F} = -a\mathbf{v} \quad (8.7)$$

where the constant aa is proportional to the absorption rate and to the detuning $\Delta = \omega - \omega_0$, where ω is the laser frequency and ω_0 is the transition frequency of the atom at rest.

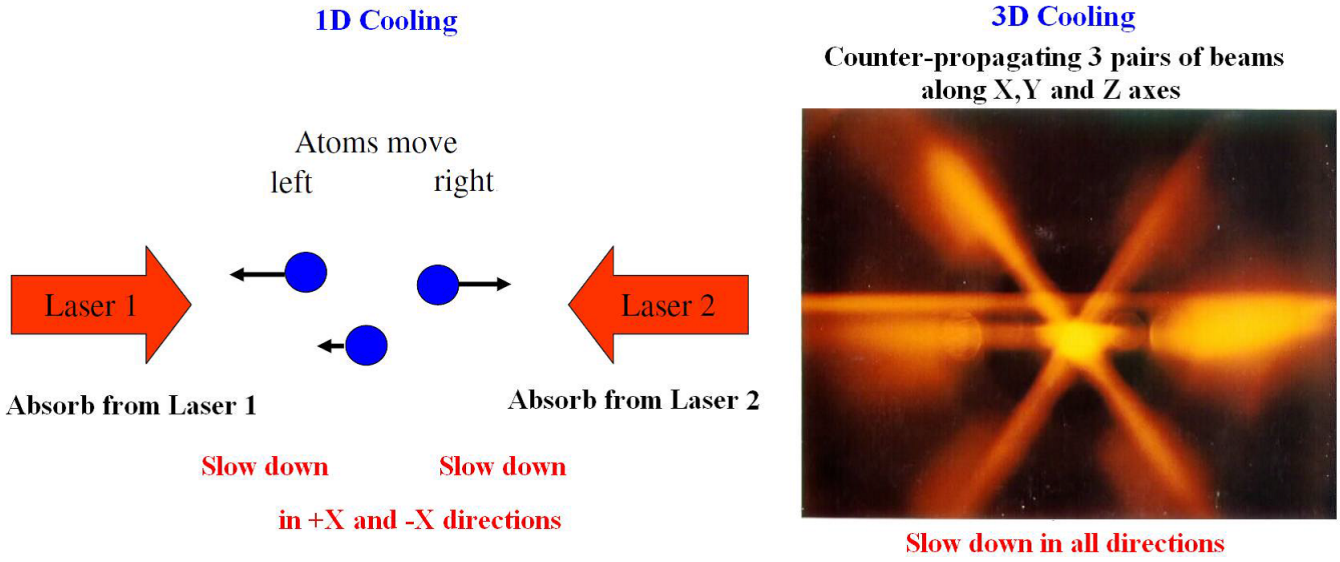


Figure 8.2

Problem 8.4

Find the average thermal velocity of a Na atom in a gas at room temperature.

The optical cooling uses the 589.16nmwavelength D_2 line corresponding to the $3P_{3/2}(F=3) \longrightarrow 3S_{1/2}(F=2)$ transition for which the spontaneous lifetime is $au_0 = 16\text{ns}$.

How many photons are to be absorbed by a sodium atom to bring it to rest?

How long does it take?

How much is the deceleration of the atom, compared with the gravitational acceleration?

What is the deceleration path length of the atom?

During the deceleration process the frequency of the pump laser has to be tuned to $\omega = \omega_0 - k\nu$, because of the Doppler shift. Here ω_0 is the circular frequency of the absorption line for an atom at rest. The required value is achieved either by tuning the exciting laser frequency, or by tuning ω_0 with a magnetic field via the Zeeman effect.

What we have discussed here corresponds to a one dimensional motion and a one dimensional cooling. In reality the atoms move in all three spatial directions which makes it necessary to apply six laser fields coming from all different orthogonal directions and achieving the deceleration of all three components of the velocity, see Fig 8.3 (b) with additional details.

Magnetooptical Trapping of Atoms

Optical cooling decreases the velocities of atoms in the atomic cloud, but that is only the initial stage of the process. In order to achieve a sufficiently deep temperature additional tricks must be applied. This can be achieved in the device called a **magneto-optical trap (MOT)**, illustrated in Fig.8.3 (a). The MOT consists of a pair of so called anti-Helmholtz coils through which a current is sent into opposite directions. With the zz-axis as the symmetry axis, the magnetic field produced by the coils in the vicinity of the trap centre at $z = 0$ is $B(z) = bz$ as it follows from the law of Biot and Savart.

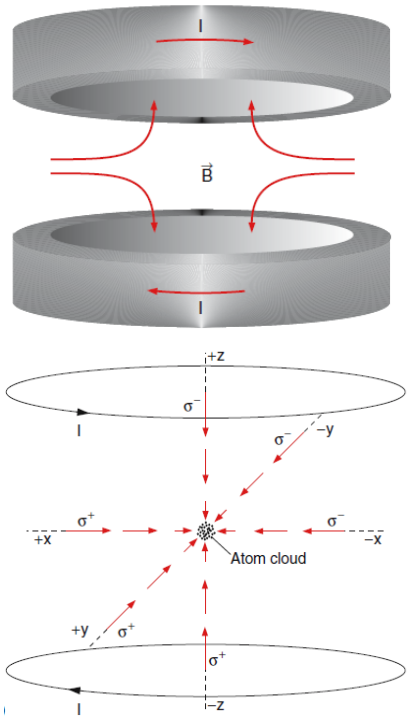


Figure 8.3:

So the magnetic field is zero at the centre $z = 0$, and increases linearly with increasing distance from the centre The field lines are indicated as red curves in Fig. 8.3 (a). In the magnetic field the atomic energy levels experience a splitting into Zeeman components with the energies

$$\varepsilon(B) = -\mathfrak{m} \cdot \mathbf{B} = g_F \mu_B m_F |\mathbf{B}| \quad (8.8)$$

Here μ_B is the Bohr-magneton, m_F is the magnetic quantum number belonging to the total angular momentum $\mathbf{F}$ (including nuclear spin) of the atom.

The six laser beams passing through the MOT are circularly polarized, carrying an angular momentum $\pm\hbar\pm\hbar$, and therefore they induce transitions with $\Delta m_F = \pm 1$. If the laser frequency ω_L is below the resonance frequency ω_0, atoms in the region $z > 0$ absorb preferentially σ_- light with negative helicity, and inducing $\Delta m_F = -1$ transitions, while for $z < 0$ mainly σ_+ light is absorbed. For $z = 0$ the absorption rates for both polarization is equal. This pushes all atoms moving outwards back towards the centre The gas of cold molecules is therefore compressed into a dense cloud around the centre of the MOT. It can be shown, that the resulting force is one that pushes the atoms from all directions towards the centre of the MOT, and the potential is like a harmonic potential trapping the atoms around the centre. Taking into account the braking force due to the Doppler effect as discussed in the previous subsection the total force acting on the atoms will be:

$$F_z = -Dz - a\nu_z \quad (8.9)$$

resulting in a damped oscillation of the atoms with mass *M* around the trap centre with a frequency and damping constant

$$\Omega = D/M, \quad \beta = a/M \quad (8.10)$$

EXAMPLE:

For Rubidium atoms with $M = 1.4 \times 10^{-25}\text{kg}$ the absorption wavelength is $\lambda = 785\text{nm}$, corresponding to $k = 8 \times 10^6 \text{m}^{-1}$. With a laser detuning $\delta = \gamma$ and an absorption rate $R_0 = \gamma/2$ one obtains $a = 4 \times 10^{-21}\text{Ns/m}$. With a magnetic field gradient $b = 0.1T/m$ and the magnetic moment $mathfrakm \approx \mu\mathbf{B}$ the constant $D = 2.37 \times 10^{-18}$ can be calculated. This gives the oscillation frequency $\omega = 4100\text{s}^{-1}$ and the damping constant $\beta = 1.2 \times 10^{-2}\text{s}^{-1}$. The atoms relax with a time constant of 12ms after about 50 oscillation periods against the trap centre. Up to now we have only regarded the movement of the atoms in the *z* direction. For the *x* and *y* directions, similar considerations hold.

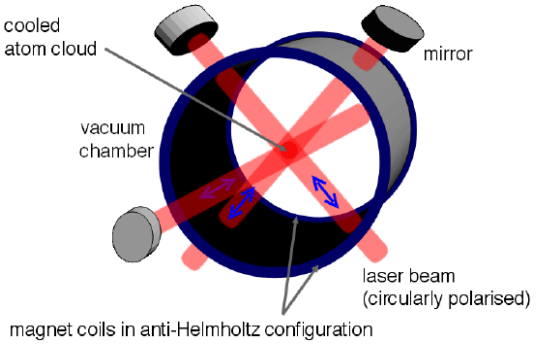


Figure 8.4: An experimental setup of a magneto-optical trap.
http://en.Wikipedia.org/wiki/File:MOT_setup.png

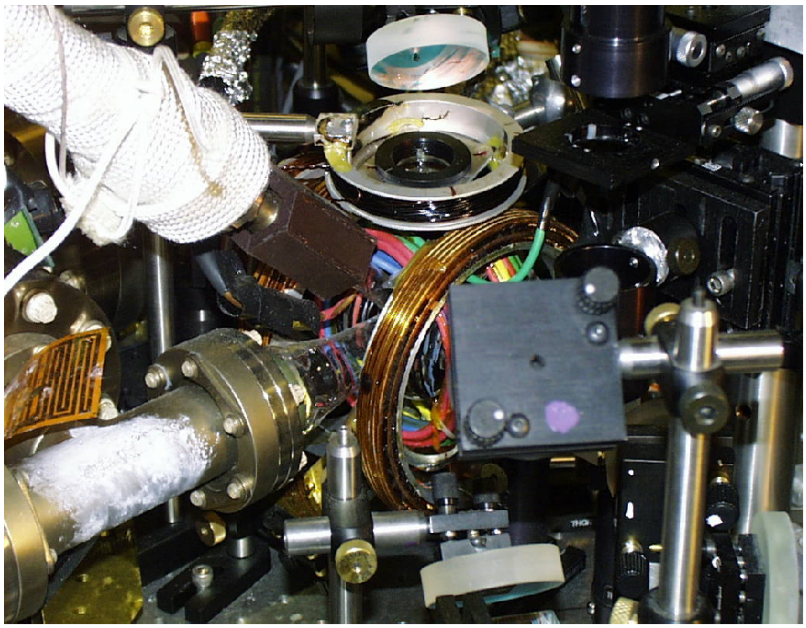


Figure 8.5: A magneto-optical trap in real laboratory situation.
http://phet.colorado.edu/hu/contributions/view/3104

Evaporation cooling

It turns out however that the temperature reached by Doppler plus magnetooptical cooling is still not low enough to reach the critical temperature for BEC. Therefore, an additional cooling technique has to be applied. This method is called evaporation cooling. It is in principle the same technique one uses for cooling a hot cup of coffee by blowing over the liquid surface. This removes the fastest molecules in the vaporous phase above the surface and decreases the average kinetic energy, i.e., the temperature of the remaining molecules.

In order to apply this technique the cold atoms are transferred from a MOT to a pure magnetic trap that has no cooling lasers, by pushing them with a laser beam into the wanted direction. In this trap that is formed by an inhomogeneous magnetic field, they are kept not by the recoil forces of lasers like in the MOT, but by the magnetic force $F = -(\mathfrak{m}\nabla)\mathbf{B}$ due to their magnetic moment $\mathfrak{m}$. Although this force is much smaller than the recoil force, the atoms, which are now already very cold, can be trapped since their kinetic energy is small. Here they have the potential energy $E_{pot} = -\mathfrak{m}\mathbf{B}$. Due to the distribution of their kinetic (thermal) energy they fill the trap potential up to a certain maximal energy E_{max}. Now the trap is irradiated by a radio-frequency wave that induces flips of the atomic spin, when its frequency $\nu_{rf} = \Delta E/h$ matches the energy difference

$$\Delta E = E_{\uparrow} - E_{\downarrow} \quad (8.11)$$

The atoms that have suffered a spin flip are automatically pushed out of the trap because their potential is now repulsive Choosing the frequency in such a way that only the hottest atoms can make a spin flip, results in a decrease of the mean energy of the trapped atoms.

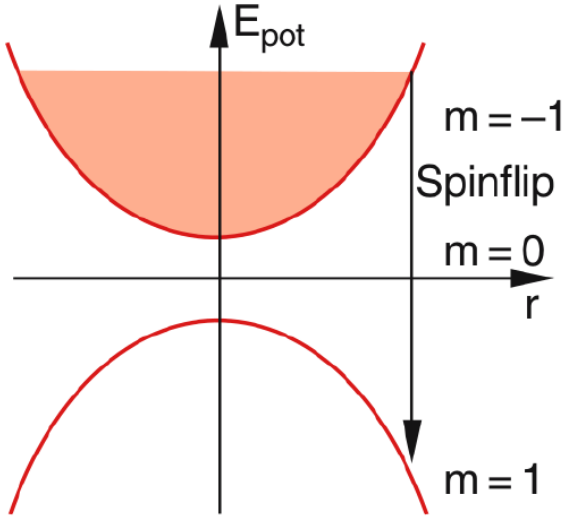


Figure 8.6: Atoms with $m = -1$ are bound in the trap, while those with $m = +1$, are not. Applying a radiofrequency magnetic field which is resonant with the transition of the highest energy atoms, will flip the spin of these and therefore release them from the trap. Tuning down gradually the frequency of this field, the level until the states are filled in is going down so finally only the lowest energy particles remain in the trap, achieving thereby the temperature where the condensation takes place.

During the evaporation of atoms, the temperature drops below the critical temperature. The radial density profile of the atoms becomes very narrow because all atoms condense into the lowest potential energy state of the magnetic trap. This can be monitored by sending a widened weak laser beam through the condensate, which is partly absorbed. With a CCD-array, the transmitted intensity is detected, which is a measure of the spatial dependence of the absorption and thus of the density of atoms.

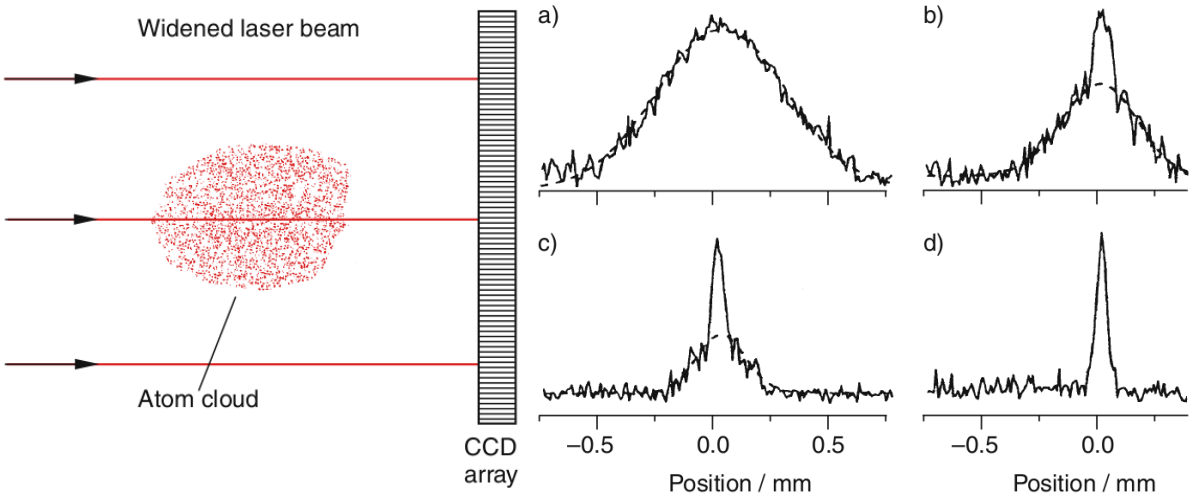


Figure 8.7: Monitoring BEC by the spatial absorption profile of the transmitted probe laser. Density profiles of atomic cloud with $T = 1.2\mu\mathrm{K}$ (a), $310\mathrm{nK}$ (b), $170\mathrm{nK}$ (c), and below the critical temperature of BEC (d)

By this technique the first experimental proof of Bose–Einstein condensation was reported in 1996 by E. Cornell and C. Wieman in Boulder, Colorado and independently by W. Ketterle and his group at the MIT in Cambridge near Boston. The group leaders received the Nobel Prize in 2001.

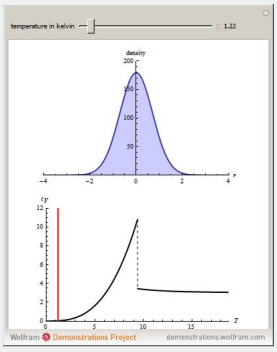
Further Reading

https://phys.libretexts.org/@go/page/50560

Under this link you can find a lot of additional information on Eric A. Cornell, Wolfgang Ketterle and Carl E. Wieman the Physics Nobel Prize winners of 2001, including interviews and their Nobel Lectures.
http://www.nobelprize.org/nobel_prizes/physics/laureates/2001/

The BEC behaves in many aspects like a supraliquid with zero viscosity. Spectroscopy of atoms in a Bose–Einstein condensate gives a lot of information on collective effects of many atoms, which are all in the same state. One of the fascinating effects is the release of a coherent beam of atoms out of the BEC. Such a coherent beam represents a large flux of atoms that all have nearly the same energy. Because of its resemblance to a coherent beam of photons, which is a laser beam, it is called an atom laser. Two beams from the same BEC can interfere with each other if they are spatially overlapping.

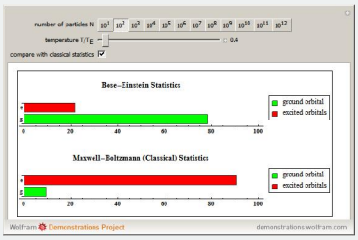
Animation



At ultra-cold temperatures, a gas of bosons undergoes a phase transition where there is a macroscopic occupation of the ground state. The top plot shows how the density profile of bosons in a 3D harmonic trap changes with temperature TT.

http://demonstrations.wolfram.com/BoseEinsteinCondensationInAHarmonicTrap/

Animation



This Demonstration shows the thermal population of the ground orbital and all the excited orbitals for a gas of N free bosons as a function of temperature. The populations according to the classical Maxwell-Boltzmann statistics can also be shown. The temperature is measured in units of Einstein's condensation temperature.

http://demonstrations.wolfram.com/BoseEinsteinCondensationFreeBosonGas/

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9: Elements of Coherent atom field interactions

Objectives

In this chapter we shall consider the dynamics of an atom under the action of a monochromatic or quasimonochromatic field. We start from first principles i.e. from the Schrödinger equation. In the second part of the chapter we consider the incoherent limit, which is important mainly in understanding the laser.

Prerequisites

The Schrödinger equation from Chapter 2. The energy of a dipole in an external electric field. Solution of differential equations. Dielectric susceptibility and its connection with the index of refraction and absorption.

Introduction

In this chapter we shall consider the dynamics of an atom under the influence of a given external, linearly polarized harmonic electric field of circular frequency ωω and amplitude E_0:

$$E(t) = E_0 \cos \omega t \quad (9.1)$$

We know, of course that an electromagnetic wave has a space dependence, as well, but as the size of an atom is about 10−310−3 times smaller than the wavelength of the field in the visible and even in the far UV domain, we can neglect the space dependence. We assume here that the field induces transition between **two resonant** energy levels, which means that there are two atomic stationary states with energies $\varepsilon_1 < \varepsilon_2$, such that their difference $\varepsilon_2 - \varepsilon_1 = \hbar\omega_0$ is **close to** $\hbar\omega$. This condition can be expressed as:

$$\omega_0 - \omega =: \Delta \ll \omega_0 \quad (9.2)$$

In the language of quantum mechanics the two levels belong to two stationary eigenstates u_1 and u_2 of the Hamiltonian H_0 of the isolated atom. We shall assume here that these levels are nondegenerate, i.e. there is only one stationary state belonging to them:

$$\begin{aligned} H_0 u_1 &= \varepsilon_1 u_1 \\ H_0 u_2 &= \varepsilon_2 u_2 \end{aligned} \quad (9.3)$$

u_1 and u_2 can be for instance the $1s$ and $2p_z$ $(m = 0)$ states of a hydrogen atom, assumed to be time independent. This is the **two-level and resonant approximation**.

If we include the interaction with the external electromagnetic wave, then the Hamilton operator must be modified:

$$H = H_0 + K \quad (9.4)$$

where *K* decribes the effect of the external field. From this point of view the atom is represented by a dipole moment operator *D* which couples the atom to the oscillating external field, and the interaction energy is

$$K = -DE = -DE_0 \cos \omega t \quad (9.5)$$

We assume here that the polarization, the direction of the electric field strength, points to the *x* direction, and accordingly *D* is the *x* component of the dipole moment. Besides being a natural assumption, this form of the interaction energy can be shown to be a very good approximation by more elaborate arguments.

Solution of the optical Rabi problem

Our task is to solve the time dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (9.6)$$

in this two dimensional problem. According to the two level resonant approximation, we shall look for the solutions as the time dependent linear combination of the two stationary states

$$\Psi(\mathbf{r}, t) = b_1(t) e^{-i\frac{\varepsilon_1}{\hbar}t} u_1(\mathbf{r}) + b_2(t) e^{-i\frac{\varepsilon_2}{\hbar}t} u_2(\mathbf{r}) \quad (9.7)$$

In (9.7) we have only two coefficients. The explicit time dependent factors $e^{-i\frac{\varepsilon_j}{\hbar}t}$ have been separated out to make the calculations more easy. In this section we assume that the amplitude of the linearly polarized electric field is constant at the position of the atom, which is assumed to be in rest.. We substitute the wave function (9.7) into (9.6) and find the equation:

$$\sum_{j=1,2}\left(i\hbar\dot{b}_j+\varepsilon_j b_j(t)\right)e^{-i\frac{\varepsilon_j}{\hbar}t}u_j=(H_0-DE_0\cos\omega t)\sum_{j=1,2}b_j(t)e^{-i\frac{\varepsilon_j}{\hbar}t}u_j \quad (9.8)$$

We can now multiply this equation by $u_i^*(\mathbf{r})(i=1,2)$, integrate with respect to the spatial coordinates of the eigenfunctions, and make use of the orthogonality condition of the stationary states, which are assumed to be normalized, as well: $\int u_i^*(\mathbf{r})u_j(\mathbf{r})d^3\mathbf{r}=\delta_{ij}$.

Then we obtain two coupled ordinary differential equations:

$$i\dot{b}_1=-\frac{dE_0}{2\hbar}\left(e^{i\omega t}+e^{-i\omega t}\right)e^{-i\omega_0 t}b_2 \quad (9.9)$$

$$i\dot{b}_2=-\frac{d^*E_0}{2\hbar}\left(e^{i\omega t}+e^{-i\omega t}\right)e^{i\omega_0 t}b_1 \quad (9.10)$$

where

$$d=\int u_1^*(\mathbf{r})Du_2(\mathbf{r})d^3\mathbf{r}=q\int u_1^*(\mathbf{r})xu_2(\mathbf{r})d^3\mathbf{r} \quad (9.11)$$

is the so called **transition matrix element** of the *x* component of the dipole moment operator, or transition dipole moment for short. As the extensions of atomic wave functions are of the order of the Bohr radius, a_0 and the charge in question is the charge of the optically active electron, q_0, the elementary charge, *d* must be of the order of q_0a_0. As an example we quote the value of dd for the $589.0\text{nm}\,D_2$ line of sodium, which is $|d|=3.5q_0a_0=3\times10^{-29}\text{Cm}$. We shall assume that

$$d=d^* \quad (9.12)$$

is a real quantity, which is very often the case. We also have taken into account here that the integrals

$$\int u_j^*(\mathbf{r})xu_j(\mathbf{r})d^3\mathbf{r}=\int x|u_j(\mathbf{r})|^2d^3\mathbf{r}=0 \quad j=1,2 \quad (9.13)$$

vanish. The reason is that for atoms the functions $|u_j(\mathbf{r})|^2$ are always even, and therefore their products with *x*, which is odd, is also an odd function. That is why atoms do not posses a permanent electric dipole moment, because these integrals are the expectation values of the dipole moment in the stationary states $u_j(\mathbf{r}$.

Close to resonance on the right hand side of Eqs. (9.9), (9.10) we have two kind of exponentials. One of them which contains the difference $\omega_0-\omega=\Delta\ll\omega$, is a slowly varying function of time if compared to the other oscillating with frequency $\omega_0+\omega\approx2\omega$. We can omit the latter ones, as on integration the terms $e^{\pm i2\omega t}/2\omega$ are small and rapidly oscillating relative to those with $e^{\pm i\Delta t}/\Delta$. This is called the **rotating wave approximation** abbreviated as RWA.

Thus with the RWA we have:

$$\dot{b}_1=i\frac{dE_0}{2\hbar}e^{i\omega t}e^{-i\omega_0 t}b_2=i\frac{dE_0}{2\hbar}e^{-i\Delta t}b_2 \quad (9.14)$$

$$\dot{b}_2=i\frac{d^*E_0}{2\hbar}e^{-i\omega t}e^{i\omega_0 t}b_1=i\frac{dE_0}{2\hbar}e^{i\Delta t}b_1 \quad (9.15)$$

It is worth to note that in the case of circulary polarized external field, when $\hat{\mathbf{E}}=E_0(\hat{\mathbf{x}}\cos\omega t+\hat{\mathbf{y}}\sin\omega t)$ we do not need the RWA, we obtain exactly the above equations.

Now we introduce the notation

$$\frac{dE_0}{\hbar}=\Omega_0 \quad (9.16)$$

which has the dimension of frequency, and describes the strength of the interaction between the atom of dipole moment dd, and field, as given by E_0.

With this notation

$$\dot{b}_1=i\frac{\Omega_0}{2}e^{-i\Delta t}b_2 \quad (9.17)$$

$$\dot{b}_2=i\frac{\Omega_0}{2}e^{i\Delta t}b_1 \quad (9.18)$$

It is easily seen that the system conserves $|b_1|^2+|b_2|^2$, which is set to be

$$|b_1|^2+|b_2|^2=1 \quad (9.19)$$

as by assumption, we have only these two levels populated.

Problem 9.1

Prove that (9.19) is valid at all times $|b_1(t)|^2 + |b_2(t)|^2$, meaning that the equations conserve the probability) if this is valid at $t = 0$, i.e. $|b_1(0)|^2 + |b_2(0)|^2$.

We shall restrict ourselves to the solution of the system of equations (9.17) and (9.18) above only if $\Delta = 0$, which is called the resonant case.

$$\begin{cases} \dot{b}_1 = i\frac{\Omega_0}{2} b_2 \\ \dot{b}_2 = i\frac{\Omega_0}{2} b_1 \end{cases} \quad (9.20)$$

The solution is the following:

$$\begin{cases} b_1(t) = b_1(0)\cos\frac{\Omega_0}{2}t + ib_2(0)\sin\frac{\Omega_0}{2}t \\ b_2(t) = ib_1(0)\sin\frac{\Omega_0}{2}t + b_2(0)\cos\frac{\Omega_0}{2}t \end{cases} \quad (9.23)$$

Assume now that the system is initially in its lower stationary state u_1. Then we can set $b_1(0) = 1$, and $b_2(0) = 0$, The probability of finding the system in the upper state is then:

$$|b_2|^2 = \sin^2\frac{\Omega_0 t}{2} = \frac{1}{2}(1 - \cos\Omega_0 t) \quad (9.26)$$

We see that this probability oscillates with the frequency Ω_0 between 0 and 1. Ω_0 is called the **resonant optical Rabi frequency** after I. I. Rabi, who first investigated the very similar phenomenon of magnetic resonance in 1938, and used it to determine experimentally the magnetic moments of atomic nuclei. We note that the Rabi frequency is usually 5 orders of magnitude smaller than the transition (Bohr) frequency.

We can see that the system reaches the upper state exactly when $\Omega_0 t = \pi$. Therefore a pulse with constant amplitude and duration of $t = \pi/\Omega_0$ is called a π pulse. On the other hand if $t = 2\pi/\Omega_0$, then the system returns to its initial ground state: this is a 2π pulse. A pulse for which $t = \frac{\pi}{2}/\Omega_0$ brings the system into an equal weight superposition of the ground and excited states: this is a $\frac{\pi}{2}$ pulse. We note that some texts use the terms for these processes as absorption till $t = \pi/\Omega_0$, and induced emission, between $t = \pi/\Omega_0$ and $t = 2\pi/\Omega_0$, but this is not really a good nomenclature. Absorption and induced emission, as they were originally introduced by Einstein are **incoherent** processes, they manifest themselves only on longer time scales, where relaxation processes play an important role, and can be considered a kind of a stationary limit of the process considered here. We shall come to this point in the next section.

This shows that on exact resonance we **can excite an atom or a system exactly to its upper state** if this excitation is so fast, that the atom can be described with the Schrödinger equation for all times. This is called a coherent excitation. It means that the atom does not interact with degrees of freedom, other then the oscillating electric field. Below we shall consider circumstances when this is not valid any more, and will complete the description with relaxation, as well as with pumping terms.

The system (9.17), (9.18) can be solved in a closed form also when $\omega_0 - \omega = \Delta eq 0$, i.e. if the system is not exactly resonant. It can be shown, that in such cases the system initially in its ground state cannot be inverted in this way any more, the probability of finding it in the state u_2 is

$$|b_2(t)|^2 = \frac{\Omega_0^2}{\Omega_0^2 + \Delta^2}\sin^2\sqrt{\Omega_0^2 + \Delta^2}\,\frac{t}{2} \quad (9.27)$$

So if $\Delta eq 0$ then the oscillation frequency is changed from Ω_0 to $\sqrt{\Omega_0^2 + \Delta^2}$, and more importantly the maximal value of $|b2(t)|^2$ is diminishing from 1 to $\frac{\Omega_0^2}{\Omega_0^2 + \Delta^2}$ with increasing Δ, i.e. with detuning the external field from the resonance condition.

As we have mentioned, the quantum theory of the resonant interaction has been derived and used first by Rabi in his molecular beam method. In that case the levels in question were magnetic spin states in nuclei, and the transition was induced by time varying magnetic fields.

In case of electronic levels in the atomic shell the transition comes from the electric dipole interaction with a time dependent electric field, as we have seen in this section. In the infrared domain the validity of these results has been proved experimentally first by G. Hocker and C. Tang in 1969, while in the visible domain by H. Gibbs with Rb atoms in 1973.

The time dependent polarization of the atom

An important quantity that can be calculated from the dynamics of the atoms is the expectation value of their dipole moment. According to quantum mechanics this can be found:

$$p(t) = \int \Psi^*(\mathbf{r},t) D \Psi(\mathbf{r},t) d^3\mathbf{r} \quad (9.28)$$

in the time dependent state $\Psi(\mathbf{r},t)$ of (9.7) as

$$\begin{aligned} p(t) &= b_1^* b_2 e^{-i\omega_0 t} \int u_1^*(\mathbf{r}) D u_2(\mathbf{r}) d^3\mathbf{r} + b_1 b_2^* e^{+i\omega_0 t} \int u_2^*(\mathbf{r}) D u_1(\mathbf{r}) d^3\mathbf{r} = \\ &= d\left(b_1^* b_2 e^{-i\omega_0 t} + b_1 b_2^* e^{+i\omega_0 t}\right) =: d\left(\varrho_{21} e^{-i\omega t} + \varrho_{12} e^{i\omega t}\right) \end{aligned} \quad (9.29)$$

Here we exploited (9.11) and that $(\varepsilon_2 - \varepsilon_1)/\hbar = \omega_0$ is the Bohr frequency of the transition. We have also introduced the definition

$$\varrho_{21} = \varrho_{12}^* = b_2 b_1^* e^{-i\Delta t} \quad (9.30)$$

which are the slowly varying factors (compared to $e^{i\omega t}$) in the atomic dipole moment. We shall give more explanation about ϱ_{21} in the next subsection. We have also assumed that the dipole matrix element (transition dipole momentum) is real, see (9.12), and we have exploited once again that the static dipole moments vanish see (9.13). Note the difference between dd and $p(t)$: d the dipole matrix element is a constant, while $p(t)$ is the time dependent dipole moment of the atom.

If the atoms constitute a gas, the macroscopic polarization density P which is an important quantity in phenomenological electrodynamics can be calculated by multiplying the expectation value of the atomic dipole moment with $\mathcal{N}$, the latter being the number of atoms per unit volume:

$$P = \mathcal{N} p(t) \quad (9.31)$$

Populations and coherences, a different formulation

Let us observe at this point that the physically interesting quantities can be expressed as products of the quantum mechanical amplitudes b_i of the levels. The probabilities of finding the atom on level *i* is $|b_i|^2$, and we shall introduce the notation for these quantities:

$$w_i := |b_i|^2 \quad (9.32)$$

The number of atoms in unit volume on level *i* is then obtained by $\mathcal{N} w_i$ which is called the population of level *i*, but frequently the probabilities w_i are also called as populations. In case of the two-level approximation above, we have always

$$w_1 + w_2 = 1 \quad (9.33)$$

therefore only one of the w_i-s is an independent variable. One usually chooses the variable

$$w := w_2 - w_1 \quad (9.34)$$

which then determines $w_1 = (1-w)/2$ and $w_2 = (1+w)/2$. w is called the population inversion, or simply inversion variable varying between −1 and 1.

The other important quantity is $p(t)$ which is determined by the products $b_i b_j^*$, or by the quantities: $\varrho_{ij} = \varrho_{ji}^*$. These are often called as **coherences between the stationary levels**. They are non-zero only if the system is in state 1, as well as in state 2 simultaneously with nonvanishing amplitudes. The ϱ_{ij}-s are responsible for the time varying polarization of the atom, and that is why an atom can radiate while it is in a superposition of its stationary states, see (9.29). Because of their direct physical meaning it is straightforward to seek the equations that determine the dynamics of $w(t)$ and $\varrho_{ij}(t)$, instead of those for the b_i amplitudes.

Using (9.17) and (9.18) this can be simply done and we present the result leaving the calculations as a problem.

$$\dot{w} = -i\Omega_0 \left(\varrho_{21} - \varrho_{21}^*\right) \quad (9.35)$$

$$\dot{\varrho}_{21} = -i\Delta\varrho_{21} - i\Omega_0 w/2 \quad (9.36)$$

Problem 9.2

Derive these equations from (9.17) and (9.18).

We note that ww is always a real number, and on exact resonance, when $\Delta = 0$, ϱ_{21} is purely imaginary, which is written customarily as $\varrho 21 = -i\nu/2$ with real ν. Then the system (9.35), (9.36) takes the simple form

$$\dot{w} = -\Omega_0 v, \quad \dot{v} = \Omega_0 w \quad (9.37)$$

An important constant of motion emerging from these equations is:

$$w^2 + v^2 = const = 1 \quad (9.38)$$

The value of the constant is 1, because it turns out to be equal to $|b_2|^2 + |b_1|^2$.

Problem 9.3

Show the validity of (9.38).

The above equality implies the following substitution

$$w = -\cos\Theta, \quad v = -\sin\Theta \quad (9.39)$$

the minus sign being a convention. The system (9.37) can be integrated even if the external field **amplitude** is time dependent $\Omega_0(t) = \frac{d}{\hbar}E_0(t)$, as from the first of the equations we have , yielding , when substituting into the second. The integral

$$\Theta(t) = \int_{-\infty}^{t} \Omega_0(t')\,dt' = \frac{d}{\hbar}\int_{-\infty}^{t} E_0(t')\,dt' \quad (9.40)$$

is called the **pulse area**. Let us note that we implicitly assumed that the time dependence of the amplitude $E_0(t)$ – called the **envelope** – is much slower than that of the rapidly oscillating phase factor cosωtcosωt, the **carrier**, i.e. $\left|\dot{E}_0(t)\right| \ll \omega |E_0(t)|$, otherwise the separation (9.1) would not make sense.

The theory outlined above forms the basis of coherent atom-field interactions, and it is very important in a large class of spectroscopic studies.

Rate equations

Relaxation terms

In the coherent interaction between atom and field considered in the previous section, we have assumed that the atom interacts exclusively with the external field. This is valid, however only for times that are short in comparison with relaxation times. The latter describe the time scale how fast (or slow) is the interaction of an atom with other degrees of freedom, which are always present as an environment, even in a perfect vacuum. So we come to the point where the relaxation and possibly pumping processes, mentioned in the introduction of this chapter must be taken into account.

The fastest of all these relaxation processes is the so called **transversal** relaxation, or phase relaxation which effects ϱ_{21} because it destroys the coherence between the levels. This is introduced here phenomenologically as an exponential decay, the time constant of which is usually denoted by T_2. This means that we compéete the right hand side of Eq. (9.36) with an additional term $-\varrho_{21}/T_2$:

$$\dot{Q}_{21} = -\frac{\varrho_{21}}{T_2} - i\Delta\varrho_{21} - i\frac{\Omega_0}{2}w \quad (9.41)$$

T_2 is characteristic of the level pair in question. In the absence of the external driving field ϱ_{21} decays exponentially due to the term $-\varrho_{21}/T_2$. The new term describes the **loss of the phase memory** between the amplitudes of the levels. For an isolated atom in vacuum this comes from the unavoidable quantum fluctuations of the electromagnetic vacuum causing spontaneous emission, and it is of the order of nanoseconds. In a laser material it is due to collisions with other atoms in a gas, or with phonons in a solid etc., and it is in the ps range, thus much faster than for an isolated atom.

If we consider only two levels and the absence of any other external agent than the coherent excitation given by $E(t)$, then we have to consider also the loss of the energy of the atoms which is transferred to its environment. This is done again by adding an additional damping term to the right hand side of (9.35) resulting also in exponential decay to the value $w = -1$, corresponding to the lower state

$$\dot{w} = -i\Omega_0\left(\varrho_{21} - \varrho_{21}^*\right) - \frac{w+1}{T_1} \quad (9.42)$$

This relaxation which is usually much slower than that of ϱ_{21} is called **longitudinal** relaxation, and

$$T_2 \ll T_1 \quad (9.43)$$

Stationary solution

The difference between the transversal and longitudinal relaxation times allows one to find a stationary solution for the ϱ_{21} variable. We can assume that due to the large value of $1/T_2$ the time derivative of ϱ_{21} can be set to zero, yielding

$$\varrho_{21} = -\frac{i}{1/T_2+i\Delta}\frac{\Omega_0}{2}w \quad (9.44)$$

Let us insert now this value in (9.42) and obtain

$$\dot{w} = -\frac{1}{T_2}\frac{1}{\Delta^2+T_2^{-2}}\Omega_0^2 w - \frac{w+1}{T_1} \quad (9.45)$$

We may introduce a dimensionless intensity

$$\mathfrak{F} = T_1 T_2 \Omega_0^2 = T_1 T_2 \left(\frac{dE_0}{\hbar}\right)^2 \quad (9.46)$$

and the Lorentzian factor:

$$\mathfrak{L}(\Delta) = \frac{1}{1+(T_2\Delta)^2} \quad (9.47)$$

so the equation takes the form:

$$\dot{w} = -\frac{\mathfrak{F}}{T_1}\mathfrak{L}(\Delta)w - \frac{w+1}{T_1} \quad (9.48)$$

This equation describes the change of the population under the effect of the field of amplitude E_0, or intensity $\mathfrak{F} \sim E_0^2$. It is not difficult to solve this equation, but instead of giving its explicit solution, we note only that the value of $w(t)$ will go exponentially to its equilibrium value w∞w∞, where $\dot{w} = 0$. This can be easily seen to be

$$w_\infty = -\frac{1}{\mathfrak{F}\mathfrak{L}(\Delta)+1} \quad (9.49)$$

which is always negative, so by incoherent excitation one cannot achieve inversion, in contrast to short time coherent excitation as we have seen it in the case of Rabi oscillations.

The incoherent process described in this section can be considered as absorption, or as induced emission, when starting from $w = +1$, in the sense Einstein introduced them originally.

Linear and stationary limit

Let us consider now the stationary solution for weak fields, where the intensity is not too strong, and the system remains close to its ground state $w = -1$ during all the process. Then the steady state solution (9.44) gives

$$\varrho_{21} = i\frac{\Omega_0}{2}\frac{1}{i\Delta+\frac{1}{T_2}} \quad (9.50)$$

while the Δ dependent macroscopic polarization is according to (9.29) and (9.31)

$$P(\Delta) = \mathcal{N}d\left(\rho_{21}e^{-i\omega t} + \rho_{12}e^{i\omega t}\right) = 2\,\mathrm{Re}\,\frac{T_2}{2}\frac{d^2}{\hbar}\mathcal{N}\frac{i+T_2\Delta}{1+(T_2\Delta)^2}E_0 e^{-i\omega t} \quad (9.51)$$

In this limiting case we have a linear relation between *P* and *E*, which we may compare with the phenomenological macroscopic connection between *P* and *E*:

\(P=\chi \epsilon_{0} E) (9.52)

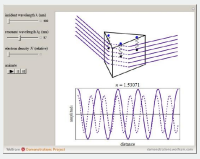
the expression

$$\chi(\Delta) = \frac{1}{\epsilon_0}\frac{d^2}{\hbar}T_2\mathcal{N}\frac{i+T_2\Delta}{1+(T_2\Delta)^2} = \chi' + i\chi'' \quad (9.53)$$

can be identified with the frequency dependent susceptibility close to resonance. We see that it has a real part, χ'\) which is known to be connected with the index of refraction via $n^2 = \epsilon' = 1+\chi'$, while its imaginary part χ'' is known to be connected to the linear absorption coefficient.

Essentially the same result can be obtained from the so called oscillator or Lorentz model of the atom, which is just the linear variant of our more precise approach. In the Lorentz model the atom cannot be inverted, which corresponds to $w = -1$ for all times.

Animation



This animation shows the relevant parameters of the Lorentz model. The index of refraction is often described as an apparent decrease in the speed of light as it passes through a dielectric medium. In fact, light photons do not actually slow down, but the effect is simulated by a retarding phase shift in the emerging electromagnetic waves. This is caused by superposition of the incident wave with a retarded wave produced by radiation from the electrons in the medium.

http://demonstrations.wolfram.com/LorentzOscillatorModelForRefractiveIndex/

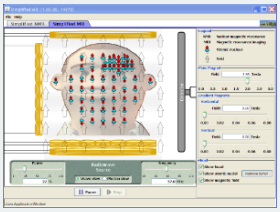
Conclusions and outlook

We presented the action of a monochromatic or (in the case of time dependent E_0) a quasimonochromatic field on atoms, that were described starting from the Schrödinger equation, i.e. from first principles. In the second part we considered the incoherent limit, which is important mainly in understanding the laser, where one has to include the space dependence of the variables, as well, which is a further complication.

The pioneer of the coherent quantum mechanical theory was I. Rabi, who applied it to magnetic resonance, and recived the Nobel prize in 1944. Interestingly, after him many other physicists obtained the Nobel for different extensions and applications of this relatively simple two-level model. Among them F. Bloch and E. Purcell (1951) for the Nuclear Magnetic Resonance (NMR) in solids. It is worth noting here that the pair of equations (9.41), (9.42) are often called optical Bloch equations. Other Nobel prizes went to C. Townes, N. Basov and A. Prokhorov (1964) for the laser principle, A. Kastler (1966), A. Schawlow and N. Bloembergen (1981) for coherent spectroscopy, N. Ramsey (1989) who was a co-worker and student of Rabi for extending the Rabi method, C. Cohen-Tannoudji, W. Phillips and S. Chu (1997) for laser cooling also based on this model, to be presented to some extent in the next section. More recently S. Haroche and D. Wineland (2012) got the prize who did experiments with single resonant two-level atoms.

The two-level resonant atomic model plays an important role in many other physical phenomena. As we have mentioned, it gives the basis of the so called semiclassical laser theory. Atomic clocks, magnetic resonance experiments, and their wide applications in chemical analysis, medical picture processing and many more are based on coherent atom field interactions.

Animation



Is it a tumor? Magnetic Resonance Imaging (MRI) can tell. Your head is full of tiny radio transmitters (the nuclear spins of the hydrogen nuclei of your water molecules). In an MRI unit, these little radios can be made to broadcast their positions, giving a detailed picture of the inside of your head.

http://phet.colorado.edu/en/simulation/mri

More recently this model got another emphasis with the emergence of the science of quantum informatics, where bits are replaced by qubits. Their most important characteristic feature is that two atomic states are not mutually exclusive, but their supperpositions can also be used for information processing, as we underscored it in this chapter.

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10: Atoms in Strong Fields

Objectives

In this chapter the excitation of atoms by intense laser pulses is discussed. This topic has grown to be one of the most exciting fields of research in atomic, molecular and optical (AMO) physics. Nowadays high-power lasers are accessible to many laboratories giving the possibility to investigate the interesting nonlinear effects which may appear.

Prerequisites

The structure of atoms. Electromagnetic field intensity, anharmonic oscillations.

Introduction

The field of research "atoms in strong laser fields" was born a few years after the invention of the laser in 1960, and has evolved considerably during the last three decades owing to the rapid technological development of high-power short-pulse lasers. Early experiments had shown that the response of an atomic system started to be nonlinear at around $I_n = 10^8 \mathrm{W/cm^2}$ for visible or near-infrared laser fields, which could be characterized by second, third or fourth order nonlinear susceptibilities. Theoretically this range can be described by the appropriate quantum mechanical method, called perturbation theory. The next important limiting intensity is $I_s = 10^{13} \mathrm{W/cm^2}$, above which the traditional quantum mechanical approaches of treating nonlinear optical processes already fails, and the interaction becomes strongly nonlinear, necessitating new concepts.

An even higher and rather obvious new limit is, when a laser field is strong enough to overcome the Coulomb forces in the atom. In order to see this, consider the field of the proton at the distance of the first Bohr radius $a0$, which is:

$$\mathcal{E}_a = \frac{|q_0|}{4\pi\epsilon_0}\frac{1}{a_0^2} = 5.1 \times 10^9 \ \mathrm{V/cm} \quad (10.1)$$

The intensity of a laser field where the oscillating electric field amplitude has the same value is:

$$I_a = \frac{1}{2}\epsilon_0 c \mathcal{E}_a^2 = 3.5 \times 10^{16} \ \mathrm{W/cm^2} \quad (10.2)$$

Problem 10.1

The intensity can also be given by the photon flux, which is:

$$\phi = \frac{I}{\hbar\omega} \quad \mathrm{photon/(s \cdot cm^2)} \quad (10.3)$$

Calculate the photon flux of a $800\mathrm{nm}$ Ti-Sapphire laser for I_a.

Experiments with intense pulses

As the most powerful laser material namely titanium-sapphire, and a new amplification technique, chirped pulse amplification, have become common around 1990, it made high-power lasers accessible to many laboratories. Since then this topic has grown to be one of the most exciting fields of research in atomic, molecular and optical (AMO) physics. A typical and general experimental setup for studying atoms in strong laser fields is shown in Figure 10.1.

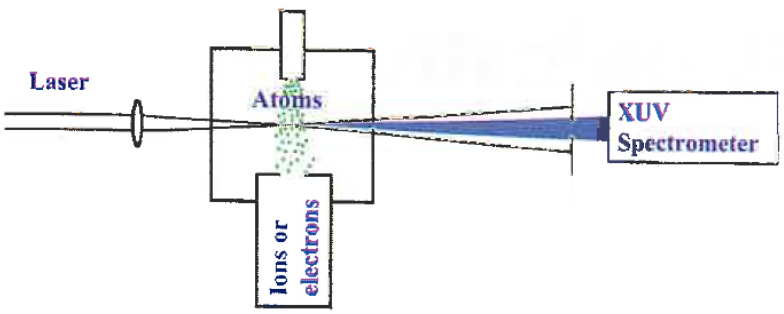


Figure 10.1: Typical schematic experimental setup in the study of atoms in strong laser fields. An intense short pulse laser is focused into an interaction chamber, which contains a gas of atoms. Ions or electrons can be detected, e.g. with time-of-flight techniques.

The first element is a short pulse laser. The laser pulses used are often in the femtosecond range, the shortest being sub-10fs. High repetition rates, today in the kHz range, allow experimentalists to get good statistics. Focused intensities needed to get into the strong field regime are of the order of $10^{14}-10^{15}\mathrm{W/cm^2}$. Since about 1995 the favourite tool has become the titanium sapphire laser, operating at $800\mathrm{nm}$ in the near-infrared, and providing very short pulse duration, high laser intensity at high repetition rate. The second part of the experimental setup is a vacuum chamber where a gas of atoms (often rare gases) is being introduced, in a cell or pulsed jet. One measures the energy of the ions generated or that of the emitted photoelectrons. In addition, angular distribution of the photoelectrons can be recorded. In high-order harmonic generation experiments, the atomic density is much higher than in ionisation experiments, pressures up to a few hundreds mbar is the usual value. The radiation emitted on axis can be detected and analysed using a standard XUV (extreme ultraviolet) spectrometer, including a grating and a photon detector.

In order to classify the strong field effects we first introduce the important quantities that can be used to describe the processes. One of them is the ionisation energy or (ionisation potential) denoted by I_P, and shown in Figure 10.2

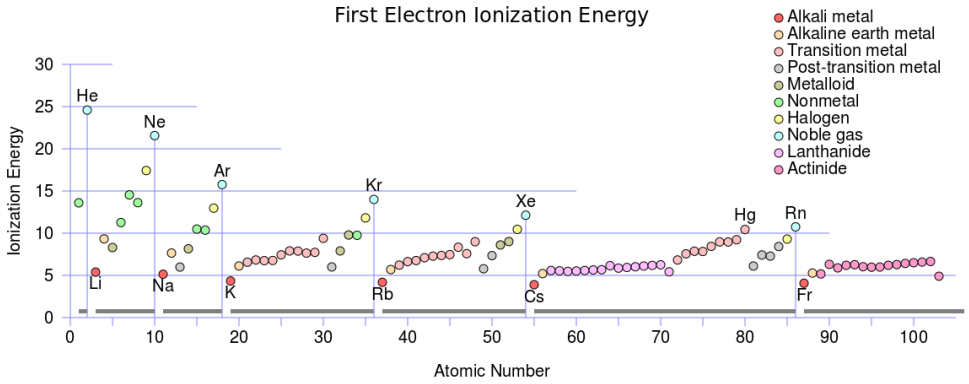


Figure 10.2: Ionization energies I_p of atoms, given here as the function of *Z*. It has the highest values for noble gas atoms, as these are the most stable chemical elements, while it is relatively small for alkali metal atoms, which have only a single electron outside a closed electron shell. The value of I_p for the H atom is $13.6\mathrm{eV}$, which is the negative of the ground state energy.
https://en.Wikipedia.org/wiki/File:First_Ionization_Energy.svg

We also introduce here the important notion of the ponderomotive potential U_P of the exciting field. It is the energy gained by an otherwise free electron in a harmonically oscillating field. A simple classical calculation shows that according to the equation of motion

$$m\dot{v} = q_0 E_0 \sin\omega t \quad (10.4)$$

the kinetic energy averaged over a period $2\pi/\omega$ is

$$\overline{\frac{1}{2}mv^2} = \frac{1}{2}\frac{q_0^2E_0^2}{m\omega^2}\overline{\cos^2\omega t} = \frac{q_0^2E_0^2}{4m\omega^2} =: U_P \quad (10.5)$$

The characteristics of the response of the atom depends on the ratio of the ionisation potential I_P and the ponderomotive potential through the parameter:

$$\gamma_K := \sqrt{\frac{I_P}{2U_P}} \quad (10.6)$$

introduced by L.V. Keldysh in 1964, and called since then the Keldysh parameter.

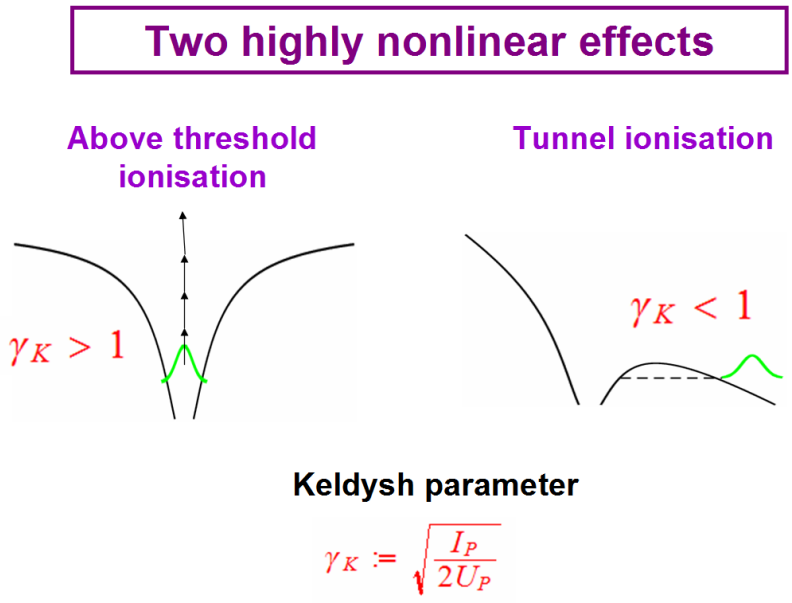


Figure 10.3: The response of the atom depends on the ratio of the ionisation potential I_P and the ponderomotive potential through the Keldysh parameter.

If the external field strength i.e. the square root of the incoming intensity is high enough then $\gamma_K < 1$ and the atomic potential can be significantly changed by that field as shown in the right hand side of the figure 10.3. The electron may then tunnel out through the potential barrier which is now the sum of the atomic and external fields. The barrier can even become lower than the energy of the bound state, then we can speak of **over the barrier ionisation**. This is valid of course for a half period of the oscillating field since the external field changes sign in the next half period and the force on the electron will change its direction to the opposite. For pulses with $\gamma_K > 1$, one observes a different process called above threshold ionisation, shown in the left hand side of the figure, and to be discussed in the next section.

Above threshold ionisation

Electrons initially in the ground state can absorb a large number of photons, many more than the minimum number required for ionisation, thus being ionised with a high kinetic energy. This new physical effect can be observed at intensities above (I_{s}=10^{13}\mathrm{W}/\mathrm{cm}^{2}\). When energy resolved photoelectron measurements have become possible in the end of the 1970s, it was observed that in the photoionization process the ejected electrons could absorb photons in excess of the minimum number required for ionisation to occur. The photoelectron spectra were seen to exhibit several peaks, separated by the photon energy $\hbar\omega$. The electron energies appear at the values

$$E_s = (n+s)h\omega - I_p \quad (10.7)$$

where *n* is the minimum number of photons to exceed the ionisation potential I_P, and $s = 0, 1, \ldots$ where ss is the number of excess photons, or above threshold photons, absorbed by the electron. This process was shown for the first time in 1979 and it was called **above threshold ionization** (ATI). A typical ATI spectrum shows a number of electron peaks separated by the laser photon energy.

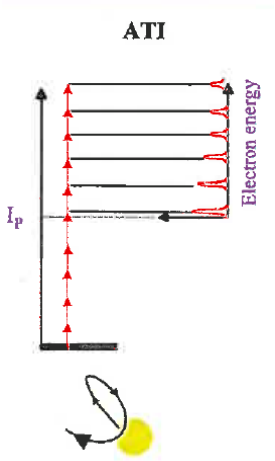


Figure 10.4:

For short and intense laser pulses, the ionisation potential I_p is increased by the (time-dependent) ponderomotive potential, i.e. the mean kinetic energy acquired by an electron oscillating in the laser field U_P. The experimental precision in detecting electron spectra increased significantly from the mid 90's owing essentially to higher laser repetition rates. Thus ATI spectra with many decades in number of counts could be recorded. Amazingly, the spectra were found to extend over many tens of eV, with a decrease for the first orders, up to $2U_p$, followed by a large plateau extending to $10U_p$. In general, with linear polarisation, electrons are generated along the polarisation's direction. It was found that angular distributions exhibit a much more complex (off-axis) structure at the edge of the plateau, called "scattering rings". The large plateau and the complex angular structure originate from the rescattering of the electron wavepacket on the parent ion.

Multiple ionisation

Not only one, but many electrons can be emitted from atoms subject to strong laser fields. Double ionisation of alkaline earth atoms was observed as early as in 1975 and the first evidence for non-sequential ionisation of rare gas atoms was first demonstrated in 1983. They can be emitted one at a time, in a sequential process, or simultaneously, a mechanism called direct, or non-sequential. The simplest multiple ionisation mechanism for atoms in strong laser fields is the so-called sequential stripping mechanism, i.e. a sequence of single electron ionisation acts: ionisation of the atom, then of the singly charged ion, then of the doubly charged ion and so on. The main experimental effort during the 1980's was to test the limits of this mechanism with the available laser powers and to understand the process responsible for the ionisation of the different charge states (multiphoton or tunnelling). It turned out however, that sequential ionisation is not the only mechanism responsible for multiple ionisation. Progress in experimental techniques with, for example, recoil-ion momentum spectroscopy and electron-ion coincidence measurements allows now scientists to record the energies and angular distributions of the electrons emitted during a multiple ionisation process, thus providing better experimental insight.

High-order harmonic generation

Another effect also observed at sufficiently high intensities was high harmonic generation (HHG). Atoms interacting with a strong laser field can emit radiation at frequencies that are high order multiples of the angular frequency of the pump laser. A high-order harmonic spectrum consists of a sequence of peaks at circular frequencies which are odd multiples of the driving, or fundamental circular frequency:

(10.8)

Only odd orders can be observed, owing to inversion symmetry in an atomic gas. In the time domain, this means that the process is periodic with a periodicity twice the laser period. A HHG spectrum has a characteristic behaviour: it shows a fast decrease for the first few harmonics, followed by a long plateau of harmonics with approximately constant intensity. The plateau ends up by a sharp cut-off. Most of the early work on harmonic generation concentrated on the extension of the plateau, i.e. the generation of harmonics of shorter wavelength. Today, harmonic spectra produced with short and intense laser pulses extend to more than 500 eV, down to the water window below the carbon K-edge at 4.4 nm. The mechanism of the generation is shown in figure 10.5.

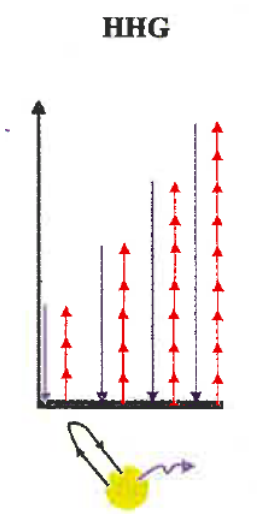


Figure 10.5:

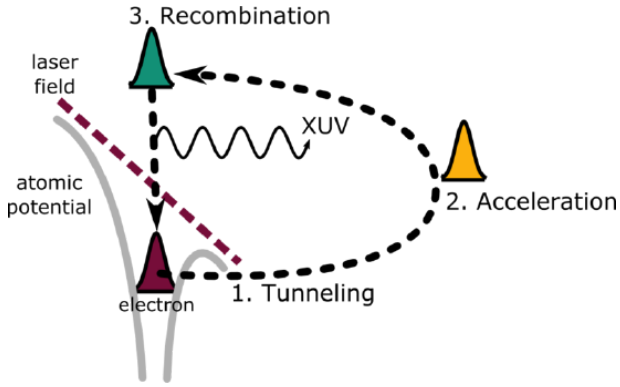


Figure 10.6: Simple illustration of the semi-classical three-step model of high-order harmonic generation. http://en.Wikipedia.org/wiki/File:ThreeStep.png

A large effort has been devoted to optimize and characterize the properties of this new source of XUV radiation. A milestone in the understanding of HHG processes was the finding by Kulander and co-workers in 1992 that the cut-off position in the harmonic spectrum follows the universal law $I_p + 3U_p$. This result was interpreted in terms of a simplified theory, called a three step model shown in figure 10.6. In the first step a tunnelling process takes place. In the second step the model neglects the Coulomb force of the core, and assumes that the electron moves only under the effect of the laser field, which first pulls away the electron from the core, but when during its oscillation it changes its sign the field may return the electron back to the core. Thirdly: when slowing down, the electron radiates in the form of harmonics whose energy comes from the energy lost by the returning electron. A realistic description of HHG must involve the calculation of the single atom response, and also the solution of propagation (Maxwell) equations for the emitted radiation.

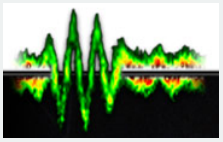
An interesting consequence of the existence of the harmonics is that among favourable circumstances they can add up and produce a sequence of peaks of pulses in the attosecond range (duration ~200 as), to be considered in the next section.

Attosecond Pulses

Almost immediately after the first observation of the harmonic plateau at the end of the 1980's, it was realised first by Győző Farkas and Csaba Tóth that, if the harmonics were emitted in phase, i.e. phase-locked, then the temporal structure of the radiation emitted from the medium would consist of a "train" of attosecond pulses separated by half the laser period. There is a clear analogy here with mode-locked lasers, where axial modes oscillating in a laser cavity are locked in phase, leading to the production of trains of short pulses. From a microscopic point of view, at each half-laser cycle, there is a short (attosecond) burst of light, as an electron recombines back to the ground state. Isolated attosecond pulses can be produced if one limits these returns to single events. The simplest idea is to use a very short (7 fs) and intense laser pulse. Such a laser source should allow one to generate single attosecond pulses, because harmonic generation occurs during a limited time interval before the onset of ionisation. Attosecond pulses have

remained, however, essentially a theoretical prediction, until 2002. Then an important experiment by the group of Agostini and Muller have shown evidence for trains of 250as pulses, while Ferenc Krausz and coworkers were able to generate isolated 650as650as pulses.

Further Reading



If you are interested in this topic check out the home page of Ferenc Krausz's group. Under the menu "Light and Matter" a lot of interesting material can be found on attosecond physics, light matter interaction etc..
http://www.attoworld.de/Mainpages/Light_and_matter/index.html

Outlook

The harmonic radiation, with attosecond pulse duration, high brightness and good spatial and temporal coherence, could be used in a growing number of applications ranging from atomic and molecular spectroscopy to solid-state and plasma physics. It has also been proposed as an alternative source for nanolithography, in particular for metrological purposes. It opens up two new fields of research: multiphoton processes in the XUV range, and attosecond physics, where processes in atoms and molecules can be studied at an unprecedented time scale. Attophysics is just born, and there is already an active discussion on the possible applications of attosecond XUV pulses. To produce routinely pulses of duration in the attosecond range is one of the main targets of the Extreme Light Infrastructure Attosecond Light Pulse Source (ELI ALPS) facility to be built up in Szeged, Hungary within the next few years.

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11: Photons: quantization of a single electromagnetic field mode

Objectives

In this chapter we introduce the concept of the photon, as the quantum of a mode of the electromagnetic field. We show that the photon number has a well defined value in an energy eigenstate of the mode. But these number states are very far from our everyday concept of a monochromatic field. Light in a highly coherent monochromatic laser field is in a so called coherent state, which we introduce shortly.

Prerequisites

lements of electrodynamics, Maxwell equations. Energy density and energy of the field. Chapter 2. The classical and the quantum harmonic oscillator (See Chapter 2).

Hamilton function of a single mode

We shall consider two perfectly reflecting parallel mirrors one at $z=0$, the other at $z=L$, and let their surface be F. We also consider a **single transversal electromagnetic standing wave** where the linearly polarized electric field oscillates in the x direction with the classical expression:

$$\mathbf{E}=\hat{\mathbf{x}}q(t)A\sin kz \quad (11.1)$$

where $q(t)$ is a time dependent function, to be determined. In order to satisfy the boundary condition that the parallel component of $\mathbf{E}$ must vanish on the surfaces of the mirrors, we obtain that k cannot be arbitrary, it must be of the form

$$k=n\pi/L \quad (11.2)$$

where $n=1,2,\ldots$. Different nn-s correspond to different k-s. Choosing one specific value of k means a specific standing wave, which is called a **mode** of the field. Let us assume that $q(t)$ is dimensionless, then A has the dimension of the electric field. According to the law of electrodynamics, a time dependent electric field is always accompanied with a magnetic field, as it follows from the Maxwell equation (Faraday's law of induction):

$$\dot{\mathbf{B}}=-\nabla\times\mathbf{E}=-\begin{vmatrix}\hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}}\\ \partial_x & \partial_y & \partial_z\\ q(t)A\sin kz & 0 & 0\end{vmatrix}=-\hat{\mathbf{y}}q(t)Ak\cos kz \quad (11.3)$$

We have then

$$\mathbf{B}=-\hat{\mathbf{y}}As(t)k\cos kz, \qquad \text{where} \qquad \dot{s}(t)=q(t) \quad (11.4)$$

where we have assumed, that the magnetic field has no static component. Then from the other Maxwell equation:

$$\dot{\mathbf{E}}=c^2\nabla\times\mathbf{B}=-c^2s(t)Ak\begin{vmatrix}\hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}}\\ \partial_x & \partial_y & \partial_z\\ 0 & \cos kz & 0\end{vmatrix} \quad (11.5)$$

we get:

$$\begin{aligned}\hat{\mathbf{x}}\dot{q}(t)A\sin kz&=-\hat{\mathbf{x}}c^2s(t)Ak^2\sin kz\\ \dot{q}(t)&=-c^2k^2s(t)=-\omega^2s(t) \quad (11.6)\\ \ddot{q}(t)+\omega^2q(t)&=0\end{aligned}$$

where the circular frequency of the mode

$$\omega=ck \quad (11.7)$$

has been introduced. The solution for $q(t)$ is

$$q(t)=q_0\cos(\omega t+\varphi_0) \quad (11.8)$$

which is well known for the standing wave.

We know that this is the solution for the position of the equation of motion of a classical linear harmonic oscillator of circular frequency ω.

Now a crucial point comes to the play. We shall consider this solution as one corresponding to a fictitious harmonic oscillator of mass M and circular frequency ω, that can be obtained from a classical Hamiltonian:

$$\mathcal{H} = \frac{p^2}{2M} + \frac{M\omega^2 q^2}{2} \quad (11.9)$$

where M is of dimension $\text{energy} \times \text{time}^2$, and p is defined as the canonical momentum by

$$p := M\dot{q} = -M\omega^2 s(t) \quad (11.10)$$

p is of the dimension of action, $\text{energy} \times \text{time}$.

Problem 11.1

Consider the Lagrange function defined as $\mathcal{L} = \frac{1}{2}M\dot{q}^2 - \frac{1}{2}M\omega^2 q^2$, and show that the canonical momentum is $p = M\dot{q}$, derive the Hamilton function and the canonical equations of motion.

Let us calculate now the energy W carried by the electromagnetic field in the cavity. This will be the volume integral of the energy density of the electromagnetic field over the cavity formed by the mirrors:

$$\begin{aligned} W &= F\int_0^L \left(\frac{1}{2}\varepsilon_0 \mathbf{E}^2 + \frac{1}{2\mu_0}\mathbf{B}^2\right) dz = \\ &= F\frac{1}{2}A^2(\varepsilon_0 q^2 \underbrace{\int_0^L \sin^2 kz dz}_{=L/2} + s^2(t)\frac{1}{\mu_0}\frac{\omega^2}{c^2}\underbrace{\int_0^L \cos^2 kz dz}_{=L/2}) = \\ &= \frac{FL}{2}A^2\frac{\varepsilon_0}{2}\left(q^2+\omega^2 s^2\right) = \frac{VA^2}{2}\frac{\varepsilon_0}{2}\left(q^2 + \frac{p^2}{M^2\omega^2}\right) = \frac{VA^2}{2}\varepsilon_0\frac{1}{M\omega^2}\left(\frac{M\omega^2 q^2}{2} + \frac{p^2}{2M}\right) \end{aligned} \quad (11.11)$$

where $V = FL$ is the volume of this cavity. If we compare this result with the form of the Hamilton function, we see that we can identify the total energy W with the Hamilton function $\mathcal{H}$, if we make the following identification.

$$M = \frac{\varepsilon_0 V A^2}{2\omega^2} \quad (11.12)$$

We see that the dynamics of a given mode is the same as that of a harmonic oscillator. In the method we applied here it is easily seen that the potential energy of the oscillator is that of the electric field, while the kinetic energy of the oscillator corresponds to the energy of the magnetic field. This analogy was realized in the end of the 19th century by Lord Rayleigh and J. Jeans, and this line of thought was also kept by M. Planck when he derived his law of the blackbody radiation. When doing so, however, he prescribed that the many modes in the cavity exchange their energy in quanta, whose energy is $h\nu = \hbar\omega$. In order to come to this point, we consider the quantum mechanics of the oscillator associated with the mode by the method above.

For sake of simplicity we have chosen here a standing wave mode, but similar considerations would hold for a **running** transverse wave, where the electric field strength is of the form:

$$\mathbf{E} = \hat{\mathbf{x}}A\left(\alpha(t)e^{ikz} + \alpha^*(t)e^{-ikz}\right) \quad (11.13)$$

Problem 11.2

Calculate the magnetic field from the Maxwell equations and derive the equation determining the time dependence of the complex function $\alpha(t)$.

Quantization of the mode

Given the Hamilton function of the field mode as an oscillator, the quantization is performed by replacing the canonical variables q and p by linear and selfadjoint operators Q and P, and stipulating the canonical commutation relations:

$$[Q, P] = i\hbar \quad (11.14)$$

where on the right hand side we have Planck's constant $\hbar = h/2\pi$, as it is required by the experimental consequences of this prescription. This method of describing the electromagnetic field mode as a quantized harmonic oscillator was the idea of P. Dirac. The mathematical step of introducing operators instead of the classical quantities results in the adequate and experimentally verified description of the quantum properties of the electromagnetic field. Note that according to the previous section Q corresponded to the electric part E, while P to the magnetic part B of the field. So the noncommutativity of these operators means that they cannot have both a sharp value in quantum electrodynamics. The energy of a single mode will be an operator, as well, and it is the Hamilton operator of the mode:

$$H = \frac{1}{2}\left(\frac{P^2}{M} + M\omega^2 Q^2\right) \quad (11.15)$$

As we know, the eigenstates of the Hamiltonian play an exceptional role in quantum theory, and we are going to determine these states.

According to their present definition Q and P do not represent coordinate and momentum in the strict sense, therefore the eigenstates of the H operators cannot be considered as functions of the q coordinate $u_n(q)$ in the ordinary sense. Therefore we turn here to a more abstract point, and we shall use the notation introduced by Dirac. A state of this quantum system will be denoted in general by the symbol $|\psi\rangle$ and the eigenstates of H by $|u_n\rangle$, called a ket. The eigenvalue equation of H can then be written as:

$$H\,|u_n\rangle = \varepsilon_n\,|u_n\rangle \quad (11.16)$$

where ε_n is a number, while $|u_n\rangle$ is the eigenket of H. In order to proceed further, we introduce the following new dimensionless operators

$$\begin{aligned} a &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{M\omega}{\hbar}}Q + i\frac{P}{\sqrt{M\hbar\omega}}\right) = \sqrt{\frac{M\omega}{2\hbar}}\left(Q + i\frac{P}{M\omega}\right) \\ a^\dagger &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{M\omega}{\hbar}}Q - i\frac{P}{\sqrt{M\hbar\omega}}\right) = \sqrt{\frac{M\omega}{2\hbar}}\left(Q - i\frac{P}{M\omega}\right) \end{aligned} \quad (11.17)$$

These are not self-adjoint, they are the adjoints of each other. It is not difficult to calculate their commutator

$$\left[a, a^\dagger\right] = \frac{1}{2\hbar}([Q, -iP] + [iP, Q]) = 1 \quad (11.18)$$

and to express the Hamiltonian in the following form:

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \quad (11.19)$$

Problem 11.3

Prove (11.18) and (11.19).

The eigenvalues and the eigenfunctions of H can be found from the eigenvalues and the eigenkets of the operator

$$N := a^\dagger a \quad (11.20)$$

It is easily seen that the eigenkets of $H = \hbar\omega(N + 1/2)$ will be identical to that of N:

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad (11.21)$$

and the eigenvalues are in the relation

(11.22)

The following theorems can be proven:

- The eigenvalues nn of $N := a^\dagger a$ are the nonnegative integers:

$$n = 0, 1, 2, \ldots \quad (11.23)$$

- To each of the energy eigenvalues εnεn there corresponds one single eigenket $|u_n\rangle$, denoted often simply by $|n\rangle$. This means that ε_n is nondegenerate

$$H|n\rangle = \hbar\omega(n + 1/2)|n\rangle \quad (11.24)$$

The ground state energy of the mode is $\hbar\omega/2$ corresponding to $n = 0$. The other eigenstates have higher energies which differ by integer multiples of $\hbar\omega$ from each other. This is the quantization of the energy in the mode, found heuristically by Einstein in 1905,

in one of his groundbreaking works about the photoelectric effect. **If the mode is in the state $|n\rangle$, we say that there are nn photons in the mode** with energy $n\hbar\omega+\hbar\omega/2$, where the ground state energy $\hbar\omega/2$ is often called as the zero point energy. We see that the value of $\hbar$ is fixed by those measurements on black body radiation and the photoeffect, which state the discreteness of the energy of the field, and the energy quanta are proportional to the (circular) frequency of the mode.

The set of states $|n\rangle$, i.e. $|0\rangle, |1\rangle, |2\rangle \ldots$ are called **photon number states**, or simply **number states of the field mode.**

- The effect of the operator $a^\dagger$ on the eigenkets is the following

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle \quad (11.25)$$

which means that $a^\dagger$ raises the state $|n\rangle$ to $|n+1\rangle$, which has an energy by $\hbar\omega$ more. We say that $a^\dagger$ **creates a photon in the mode, $a^\dagger$ is called therefore a raising or a creation operator**. The numerical factor $\sqrt{n+1}$ is introduced for convenience, it is actually a normalization constant.

- The effect of the operator aa on the eigenkets is the following

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (11.26)$$

which means that aa lowers the state $|n\rangle$ to $|n-1\rangle$, which has an energy by $\hbar\omega$ less. We say that aa **annihilates a photon in the mode, a is called therefore a lowering or an annihilation operator**. Once again the numerical factor $\sqrt{n}$ is introduced for convenience, it is actually a normalization constant.

- The state $|n=0\rangle := |0\rangle$ is the lowest energy state, or ground state called often the **vacuum**. According to (11.26)

$$a|0\rangle = 0 \quad (11.27)$$

where the 0 on the right hand side is not a state. This just means that there are no states with energy below the **vacuum**.

Problem 11.4

Using (11.26) and (11.25) show the validity of the eigenvalue equation (11.21) of $N = a^\dagger a$.

Problem 11.5

Prove that a number state can be created from the vacuum according to the formula

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle \quad (11.28)$$

Other states of the field

The photon number states are very important in quantum electrodynamics, but they are only an exceptional set. There are several other quantum states of a single mode. It can be proven, however that any state characterizing the field can be expanded in terms of the number states, as a generally infinite linear combination of them:

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|n\rangle \quad (11.29)$$

where we require the equality $\sum_{n=0}^{\infty} |c_n|^2 = 1$. It turns out that the actual generation of number states in a cavity mode is a very difficult experimental task.

The time dependence of the state expanded in terms of the number state follows from the general rules of quantum mechanics, and it is given by:

$$|\Psi(t)\rangle = \sum_{n=0}^{\infty} c_n e^{-i(n+1/2)\omega t}|n\rangle = e^{-i\omega t/2}\sum_{n=0}^{\infty} c_n e^{-in\omega t}|n\rangle \quad (11.30)$$

where we put into the exponentials the energy eigenvalues belonging to the given stationary state $|n\rangle$.

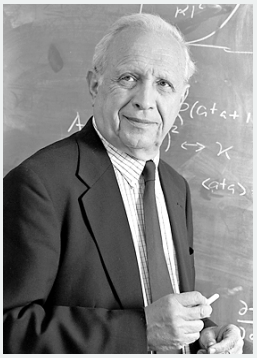
Coherent states

We note here that the states that are most close to our everyday concept of a monochromatic field mode, are not the number states. The light in a highly coherent monochromatic laser field, say that of a red He-Ne laser at 632.8nm is in a so called coherent state of the mode. The coherent states are labelled by a complex number, denoted usually by α, the state itself is then $|\alpha\rangle$, which has the following expansion in terms of the number states:

$$|\alpha\rangle = \sum_{n=0}^{\infty} e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} |n\rangle \quad (11.31)$$

We stress that α is an arbitrary complex number. The coherent states are not eigenstates of the mode Hamiltonian and of N, therefore the number of photons has not a well defined value in them. Coherent states of an oscillator have already been introduced by Schrödinger in the very early days of quantum mechanics. The use of the coherent states in photon optics was initiated by R. Glauber (Nobel prize 2005).

Further Reading



Under this link you can find the Nobel Lecture of Roy Glauber with the title: One Hundred Years of Light Quanta.
http://www.nobelprize.org/nobel_prizes/physics/laureates/2005/glauber-lecture.html

Problem 11.6

Prove that the coefficients in this expansion obey the condition $\sum_{n=0}^{\infty} |c_n|^2 = 1$.

The intensity of the field turns out to be proportional to $|\alpha|^2$, which is the expectation value of the photon number in the coherent state: .

The operators of field strengths

Now we come back to the electric and magnetic fields in the mode. In the expression (11.1) we replace the classical amplitude qq by its quantum counterpart, by the Q operator. Using the expression of Q by a and $a^\dagger$, and the identification (11.12): ($\frac{\varepsilon_0 V A^2}{2\omega^2} = M$) we get:

$$\mathbf{E} = \hat{\mathbf{x}} Q A \sin kz = \hat{\mathbf{x}} \frac{a+a^\dagger}{\sqrt{2}} \sqrt{\frac{\hbar}{M\omega}} A \sin kz = \hat{\mathbf{x}} \left(a + a^\dagger\right) \sqrt{\frac{\hbar\omega}{\varepsilon_0 V}} \sin kz \quad (11.32)$$

In this way the electric filed strength has become an operator. Similarly the magnetic field is obtained by using the quantum variant of $s = -p/\left(M\omega^2\right)$

(11.33)

Interestingly the perpendicular components of the $mathbf{E}$ and the $\mathbf{B}$ fields do not commute with each other, except at the points in space where the fields are zero:

$$\begin{aligned} \mathbf{B} &= -\hat{\mathbf{y}} A S k \cos kz = \hat{\mathbf{y}} A \frac{P}{M\omega^2} \frac{\omega}{c} \cos kz = \hat{\mathbf{y}} A \sqrt{\frac{M\hbar\omega}{2}} \frac{1}{M\omega^2} \frac{\omega}{c} i \left(a^\dagger - a\right) \cos kz = \\ &= \hat{\mathbf{y}} A \sqrt{\frac{\hbar}{2M\omega}} \frac{1}{c} i \left(a^\dagger - a\right) \cos kz = \hat{\mathbf{y}} \sqrt{\frac{\hbar\omega}{\varepsilon_0 V}} \frac{1}{c} i \left(a^\dagger - a\right) \cos kz \end{aligned} \quad (11.34)$$

Concluding remarks

We have considered in this section the simplest way to introduce the correct notion of the photon, which can be considered as the amount of the excitation of a field mode. The photon number has a well defined value in an energy eigenstate of the mode. There are however many more other interesting states of a mode, which could be created and detected in experiments. One of the most

important among them is the coherent state, which we introduced shortly. Number states, coherent states, as well as other, more complicated ones have also practical applications in high precision measurements performed by light waves and in other technical fields, too. Another important point here is that a cavity or free space can sustain, of course, a great number of modes, instead of one. These modes may have identical or different frequencies, and their number in a frequency interval is an important parameter of the given physical situation. The extension of the theory to multimode fields and the discussion of other possible states is the realm of quantum optics, which could be a subject of another full semester course.

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12: A quantum paradox and the experiments

Objectives

Quantum mechanics makes probabilistic predictions about the possible outcomes of an experiment with microscopic objects, particles. This is a statistical statement concerning many particles. One can assume that there exists a deeper non-statistical, i.e. deterministic law for single particles predicting what should happen with that specific particle.

Is there any deeper theory or law determining the experimental result with certainty? There must be such a theory according to Einstein, implying that quantum mechanics cannot be a complete theory. On the other hand, according to Bohr – who was another founder of quantum theory – there is no place for a deeper theory, we cannot predict anything more about a single particle, but probabilities.

Prerequisites

Chapter 1. Polarization of plane light waves in classical optics.

The EPR-paradox, Bohm's version

In this last section we consider certain principal questions of quantum mechanics that are connected with the very essence of the subject, i.e. with the nature of the probabilities appearing in the theory. In classical physics a measurement makes a **record of the value** of a physical quantity of a particle, a body, or a system which is assumed to be a property of the particle that existed prior to the measurement, and independently whether we measure it or not. In contrast to this, in quantum physics – a set of particles can be prepared to have exactly the same property from a certain point of view, still they can show up quite different measurement results, from the point of view of another property.

The simplest example is connected with light polarization, or stated in quantum language: photon polarization. According to quantum mechanics **if a plane transversal wave is polarized, and its plane of polarization makes an angle θ with another polarization direction, then the photons in the beam are polarized also in that latter direction with a probability amplitude** $cos\theta$. This means, for instance, that if the polarization makes an angle θ with the horizontal direction and therefore an angle $\pi/2-\theta$ with the vertical direction, then the corresponding probability amplitudes are $cos\theta$ and $cos(\pi/2-\theta)=sin\theta$, respectively. According to the fundamental role of quantum physics the probabilities are in turn the (absolute value) squares of the amplitudes. So the probability of finding a single photon of the original beam to be polarized horizontally is $cos^2\theta$ while the probability of being vertically polarized is $sin^2\theta$. This law is easily verified already with a classical plane wave field of intensity I_0 which is polarized so that it makes an angle θ with the horizontal direction. The beam is directed to a calcite crystal which separates it into two beams so that one of them is polarized horizontally the other one vertically – these are the **eigendirections** of the calcite – and the two beams are distinct, so that they can be checked individually. Then the intensity of the horizontally polarized beam after the calcite will be $I_0cos^2\theta$, while that of the vertically polarized beam will be $I_0sin^2\theta$. As the intensity is proportional to the number of photons, this is a proof of the probability law. Present day technique allows also to check the probabilities themselves, because photons can also be detected one by one by sensitive detectors.

It will be important that we can set the calcite so that its eigendirections are not horizontal and vertical, which we shall call setting *A* later on, but also in a way, say *B* or *C*, so that the two eigendirections are different from those of the setting *A*. Let us note, however, that the two eigendirections are always orthogonal to each other.

The following question arises: what determines the final polarization direction of the photon. According to quantum mechanics the photon **becomes** vertical, or horizontal **during the interacion** with the measurement apparatus. This is not encoded in the incoming particle, therefore it is principally impossible to answer the question with certainty, most we can say are the probabilities of the two different possible outcomes. Stated in another way, the measurement does not establish a previously existing property of the photon, rather it is the measurement itself that creates the property with the appropriate probability.

This answer, however, does not satisfy everybody, because one can imagine a different answer, as well, namely assuming that for each photon both properties did exist before the measurement, i.e. it was polarized in say 45° and **at the same time** it had the property of being horizontally polarized, if we obtained the latter result during the measurement. It is another question that quantum mechanics does not give account of both properties simultaneously, as it cannot give with unit probability – i.e. with complete certainty – the direction of polarization of a single photon for **two** non-parallel or nonorthogonal directions. This would

mean then that there exists a kind of a theory, deeper than quantum mechanics, according to which these properties are present simultaneously and exactly in the measured object. From the point of view of quantum theory the parameter that would give the result with certainty is not present, so it is a hidden parameter as it is called in these theories.

As quantum mechanics does not give account of these parameters, it cannot be a **complete** description of physical reality. This was the point of view of A. Einstein, and this was exposed in the most perplexing way in the famous paper by A. Einstein, B. Podolsky and N. Rosen in 1935: "Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?" In the end of the work they came to the conclusion that quantum mechanics is not complete, but they add that such a theory shall appear in the future.

In the beginning the authors of the EPR paper try to give an exact definition what they consider a complete theory:

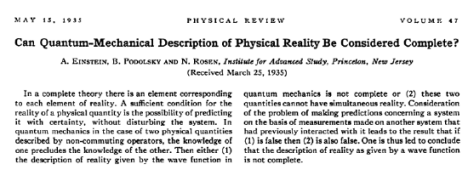
> *"A theory is complete if every element of physical reality has its counterpart in the physical theory."*

But what is an element of physical reality? They give the following answer:

> *"If, without in any way disturbing a system, we can predict with certainty (i.e., with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding lo this physical quantity."*

Einstein, Podolsky and Rosen (EPR) present the description and the analysis of an imagined experiment, (so called Gedankenexperiment) performed on a pair of quantum particles, which according to the authors shows that quantum mechanics is not a complete theory in the sense they require it. In their example they consider the measurement of the positions and the momenta of a pair of particles, which emerge in a disintegration process. Instead of that it is simpler to consider another variant of the experiment, when it is done with a pair of two-state systems, as there are only two possible results in a single measurement apparatus, instead of the infinitely many possible outcomes when measuring position or/and momenta. Such a variant of the EPR paradox was proposed by David Bohm in 1957 with pairs of spin 1/2 particles, or what we shall analyze, with photons having two orthogonal polarization eigenstates.

Further Reading



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Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?

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In a complete theory there is an element corresponding to each element of reality. A sufficient condition for the reality of a physical quantity is the possibility of predicting it with certainty, without disturbing the system. In quantum mechanics in the case of two physical quantities described by non-commuting operators, the knowledge of one precludes the knowledge of the other. Then either (1) the description of reality given by the wave function in quantum mechanics is not complete or (2) these two quantities cannot have simultaneous reality. Consideration of the problem of making predictions concerning a system on the basis of measurements made on another system that had previously interacted with it leads to the result that if (1) is false then (2) is also false. One is thus led to conclude that the description of reality as given by a wave function is not complete.

You can download the original EPR paper under this link:
http://prola.aps.org/pdf/PR/v47/i10/p777_1

The essential features of the experiment, performed many times since Bohm's proposal, are the following. A special source generates pairs of photons, such that the members of the pair propagate in different spatial directions, say, one to the left, the other to the right. The polarization properties of the members are measured independently. One places two polarization measurement devices perpendicularly to the propagation of the beams. These are e.g. calcite crystals in the paths of the two photons which pass through them, and measure the polarization properties of the photons. The devices can be set making different angles with the horizontal direction. The possible settings of the devices will be denoted by different capital letters A, B, C and the two corresponding eigenstates of the devices by $A+$ and $A-$; $B+$ and $B-$; and $C+$ and $C-$ respectively. With an appropriate photon source one can achieve that there is a strict anticorrelation in the measurement between the members of a pair, which means the following. Assume that the devices are set identically, on both sides of the source. Then both photons pass through the same type of device, say horizontal-vertical, to be denoted by A. One observes then that if one of the photons is polarized horizontally $A-$ on the left, its pair turns always out to be vertically polarized $A+$, on the right, or vice versa. The same thing happens if both polarizers are set in any direction say B which is different from A, but identical for both photons. If $B+$ denotes 60° from the horizontal and $B-$ means -30° from the horizontal, then if one of the photons comes is polarized in $B+$, its pair will be $B-$, or

the other way round. Thus the polarization states of a given member are always orthogonal to each other. Such pairs of particles are called EPR pairs. This anticorrelation of the pair follows from the way one creates them, which will be detailed below.

An EPR state of a photon pair is:

$$\psi = \frac{1}{\sqrt{2}}\{(A+)_1(A-)_2 - (A-)_1(A+)_2\} \quad (12.1)$$

where subscript labels the particle: 1 goes to left and 2 to the right. The first term in the state above says that photon 1 is polarized vertically, while photon 2 is polarized horizontally. The second term means all this the other way round. What is important, quantum mechanics allows the superposition of the two possibilities. We have already encountered a similar state when we considered the spin singlet state of the two electrons in the H_2 molecule in Chapter 7.

Problem 12.1

Show that the state (12.1) above cannot be written as a product of two one-particle states.

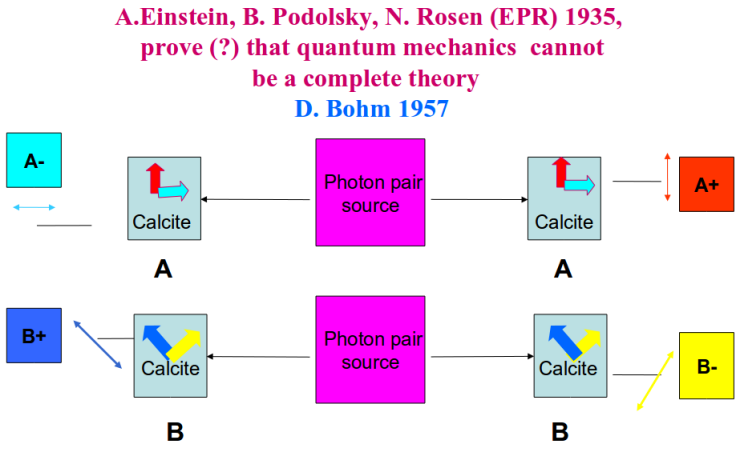


Figure 12.1: Two possible eigenstates of the polarizer A are denoted by $A+$ and $A-$. The same notation is used in case of polarizer BB, the two eigenstates are $B+$ and $B-$. There is a strict anticorrelation between the outcomes on the two sides, if the devices are set identically

But then it is sufficient to measure only on one photon of the pair. We may think that we know the result for the other member, even without doing the measurement, because it will be always opposite to the one for its partner. Therefore without disturbing it, we can predict its value, thus it is the element of reality according to EPR. One has to add here, that it is impossible that we measure a value $A+$ on the left **because** we measured $A-$ on the right. The propagation of this information needs time, but the two events can have a **space-like separation** (in the sense of relativity theory), which means that only a signal faster than light could influence the result of the measurement on the other side, depending on the result of one of the sides. This is the locality principle emphasized so much by Einstein's theory of relativity. To conclude: the polarization property of the unmeasured photon is the element of reality, and a complete theory must assign a well defined value to it in the sense defined by EPR.

But there is even more than that: in the case of the EPR pair we can tell the state of a particle exactly even from the point of view of two incompatible devices, what is impossible in quantum mechanics, in principle. Let us put two different devices on the two sides.

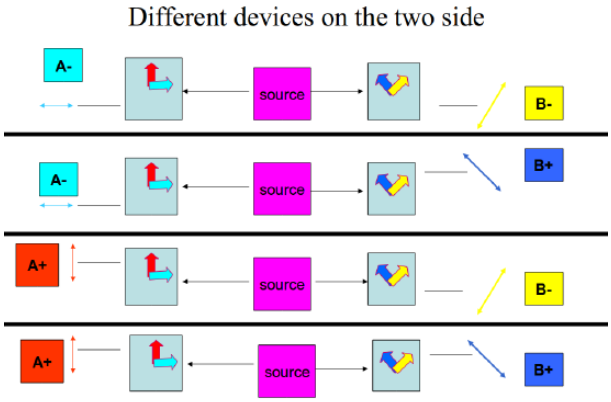


Figure 12.2:

If we measure on the left side the property A (physical quantity), then we also know the state of its pair on the right from the point of view of A, due to the perfect anticorrelation. It will be perpendicular to the direction measured on the left. But at the same time on the right we may measure with another type of apparatus, that measures the property B. In this way we can state both properties of the given particle, one of them follows from the measured value on its mate on the left, the other one is measured actually. The same is true for its partner. This would mean that both properties are well defined in the case of a single particle, while according to QM this is impossible, if A and B have different eigendirections as seen in figure 12.2. In quantum mechanics only the probability amplitude and a corresponding probability is given if A and B make an angle different from 0° or 90°. This reasoning led EPR to the conclusion that QM, which does not give account for two incompatible elements of physical reality, cannot be complete. In contrast to the statement by EPR, N. Bohr argued that the two particles are part of a single unseparable quantum system, according to the present wording they are in an **entangled state**, therefore a measurement on one of its parts immediately influences its other part, even if they are very far from each other let the two measurements two spacelike events in the sense of special relativity. But this statement contradicted to one of the most fundamental principles of physics, locality. Therefore Einstein could not accept Bohr's arguments and the debate and the paradox remained unsolved for about 30 years.

Bell-inequalities with photons

In order to decide the question, John Bell proposed an explicit experimental arrangement in 1964. One has to measure not two but three different quantities (orthogonal polarizations) A, B, and C for the photon pairs, so that the three possible settings of the polarizers are chosen randomly and independently from each other. It turns out, that based on the experimentally measured number of pairs one can decide whether quantum mechanics, or the Einstein hypothesis is correct, the latter saying that the particles must have well defined polarizations in different directions simultaneously. The original idea of Bell will be presented here as it was discussed by Eugene Wigner.

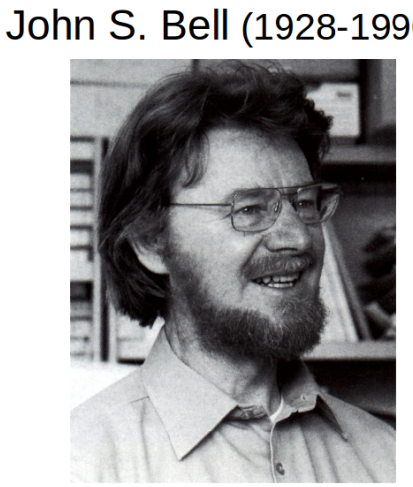


Figure 12.3:

Assume that the members of the pair had a well defined polarization before the measurement: $+$ or $-$ in each of the three directions *A*, *B*, and *C*. As the measurements show, in a single pair the polarization of the two particles are always orthogonal to each other, shown up explicitly if we use the same settings on both sides. The possible 8 types of the pairs are shown in table 12.1, and let us denote the measured number of a given type of pairs by N_k.

	left side			right side		
	A	*B*	*C*	*A*	*B*	*C*
N_1	+	+	+	−	−	−
N_2	+	+	−	−	−	+
N_3	+	−	+	−	+	−
N_4	+	−	−	−	+	+
N_5	−	+	+	+	−	−
N_6	−	+	−	+	−	+
N_7	−	−	+	+	+	−
N_8	−	−	−	+	+	+

Table 12.1:

Let us consider now the pairs for which the particle going to left resulted in $A+$, while the one going to right came out as $C+$. These events will of course be present only if the device on the left was set to *A* while the one at right was set to *C*. The number of such pairs shall be denoted here by $N(A+, C+)$, and according to the table above $N(A+, C+) = N_2 + N_4$. Similarly the number of pairs for which we got A+A+ on the left and B+B+ on the right the result is $N(A+, B+) = N_3 + N_4$. Finally the number of those where we had $B+$ on the left and $C+$ on the right was $N(B+, C+) = N_2 + N_6$.

According to the simple inequality

$$N_2 + N_4 \leq (N_3 + N_4) + (N_2 + N_6) \quad (12.2)$$

valid because by definition all the numbers N_i are nonnegative integers, we get:

$$N(A+, C+) \leq N(A+, B+) + N(B+, C+) \quad (12.3)$$

It is important that the number of pairs $N(A+, C+), N(A+, B+), N(B+, C+)$ can be measured, and the experimental result can be compared with the inequality obtained above. Before going on, however, we reformulate the inequality (12.3) into probabilities, in order to compare it with quantum mechanics, which give its results in terms of probabilities.

Let $P(A+, C+)$ the probability, that by choosing randomly the directions we set on the left the device to *A*, and it measured a result $A+$, while the measurement on the right particle happened again by random choice in the direction *C*, and resulted in $C+$. Then

$$P(A+, C+) = \frac{N(A+,C+)}{\sum_{i=1}^{8} N_i} \quad (12.4)$$

and similarly $P(A+, B+) = \frac{N(A+,B+)}{\sum_{i=1}^{8} N_i}, P(B+, C+) = \frac{N(B+,C+)}{\sum_{i=1}^{B} N_i}$, if we made sufficiently many measurements. Accordingly the inequality (12.3) can be written as

$$P(A+, C+) \leq P(A+, B+) + P(B+, C+) \quad (12.5)$$

This is a Bell inequality, which – as we must remember – was derived by using the assumption that the pairs had well defined properties before the measurement was performed. There were no quantum mechanical arguments in obtaining it.

So let us look at what QM says about the probabilities occurring in (12.5) as shown in the figure below. In a real measurement one has identical crystals on both sides, and they are rotated randomly and independently of each other in three directions *A*, *B* and *C*. If on the left side we measure $A+$ for instance, then its pair should be in state $A-$. But we measure say *C* on it, and the result measured on the partner can be either $C+$ or $C-$. The probability amplitude of getting the result that this other particle is polarized in the direction $\hat{e}_\theta$ is $cos\theta$, where θ is the angle with $A-$. The corresponding probability is thus $cos^2\theta$. Or we wish to express it

with the angle made with $A+$, which is $\alpha = \pi/2 - \theta$, then the probability is $sin^2\alpha$. Choosing randomly the possible three directions on both sides with equal probabilities $1/3$, the probability of all the possible settings of the pair of the apparatuses equals to $1/9$. The probability of obtaining say A+A+ on the left before we measured on the right is $1/2$, then with a given setting of both crystals the probability is e.g. $P(A+, C+) = \frac{1}{18}\sin^2(A+, C+)$, where $(A+, C+)$ denotes here the angle between the directions $A+$ and $C+$.

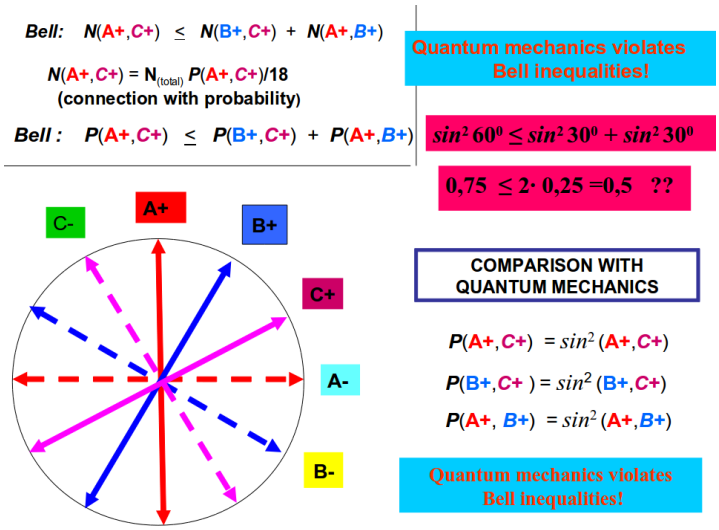


Figure 12.4: Violation of Bell inequality

Let us choose specifically the directions shown in the figure, i.e. let the eigendirections of *A*, *B* and *C* be rotated consecutively by 30°. In other words we choose $(A+, B+) = (B+, C+) = 30^\circ$ and $(A+, C+) = 60^\circ$. Then the quantum mechanical probabilities give the following result:

$$P(A+, C+) = \tfrac{1}{18}\sin^2 60^\circ, \quad P(A+, B+) = \tfrac{1}{18}\sin^2 30^\circ, \quad P(B+, C+) = \tfrac{1}{18}\sin^2 30^\circ \quad (12.6)$$

If we substitute these probabilities into (12.5) we observe that these results do not obey it, because that would require the fulfilment of $\sin^2 60^\circ \leq 2\sin^2 30^\circ$, i.e. the inequality

$$\tfrac{3}{4} \leq \tfrac{1}{2} \quad (12.7)$$

which is obviously false.

This means that by choosing appropriate directions for the crystals the corresponding quantum mechanical probabilities violate the Bell inequality. This turns out to be then an experimental possibility to decide whether quantum mechanics or Bell inequalities are valid in the real physical world. **According to the experiments measuring directly the numbers $N(A+, C+)$ etc. it turned out that the Bell inequalities are not valid for appropriately chosen directions *A*, *B*, and *C* as above but the results are in agreement with the predictions of QM.**

All this should mean that in the derivation of the Bell inequalities must be something that contradicts to what is in the real physical world. There are two possibilities of errors. One of them could have been that filling out the table 12.1 we assumed that a particle, and its partner possessed two, (actually three) different polarization properties already before the measurement, they did exist in them independently of the measurement that was performed on them later. The other possible error could be that there is a nonlocal communication between the two members of a pair, i.e. the measured state of one of the particles depends on the measurement on its distant partner. (However one can show, that information cannot be transmitted in this way with a speed faster than light, because information transfer would necessitate an additional classical communication channel, and the speed of the transfer is determined by the velocity of the classical signal. That means that locality is not violated in this sense). Both possibilities, as reasons of the discrepancy, contradict to traditional concepts about the natural world. In the first case it contradicts to the assumption that all the possible properties of a particle, including the incompatible properties, have a well defined value before and independently of the measurement. This assumption is usually called as **realism**. The second possibility contradicts to **locality**, in the sense that the measurement result influences instantaneously a distant, spatially separated other measurement.

Experiments and Bell inequalities

The first experiments about validity or violation of the Bell inequalities was performed by J. F. Clauser and co-workers in 1972. A later experiment by A. Aspect (1982) was the first, where the settings of the two crystals were made so that the separation of these two events was space-like, i.e. a light signal imagined to start from one of the crystals at the time of its measurement could not reach the other one before it measured the state of the other particle.

Here we show the setup of the experiment of A. Zeilinger (1995) where the pair of photons emerged from a nonlinear crystal.

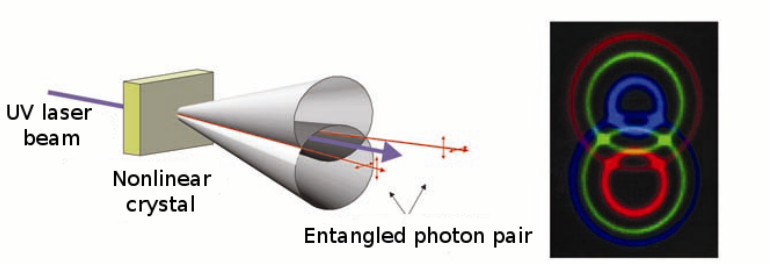
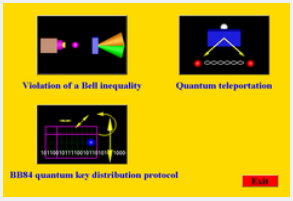


Figure 12.5: Generation of an entangled photon pair. (In the figure colours are fictitious, green colour corresponds to the infrared photons of wavelength 702 nm.)

When the photons of an UV laser of wavelength 351 nm pass through the nonlinear crystal, a small part of them are split into two photons with smaller energy and thus with smaller frequency. This process is called parametric down conversion in nonlinear optics. The emerging two beams leave the crystal along the superficial of two cones, satisfying the energy and momentum conservation. Among the pairs some will share equally the original energy and momentum, their wavelength will be identically 702 nm (this is called the degenerate case). With an appropriate setting of the crystal one can achieve that the polarization of the members are always orthogonal to each other, as assumed for the EPR pair in the discussion above. In this latter case the angle at the apices of the two cones are identical and along their intersection – at the two green spots in the simulated figure on the right hand side of figure 12.5 – the photon pairs will have just the required property.

Animation



Downloading and running the exe file we can chose from three simulations. The first one demonstrates the violation of Bell inequality. The second one shows quantum teleportation, while the third is a realization of the BB84 quantum key distribution (QKD) protocol (not discussed here).

http://titan.physx.u-szeged.hu/~mmquantum/download.php?download_file=Qmdemo.exe

Experiments unanimously proved the validity of the quantum mechanical result and the violation of the Bell inequalities.

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